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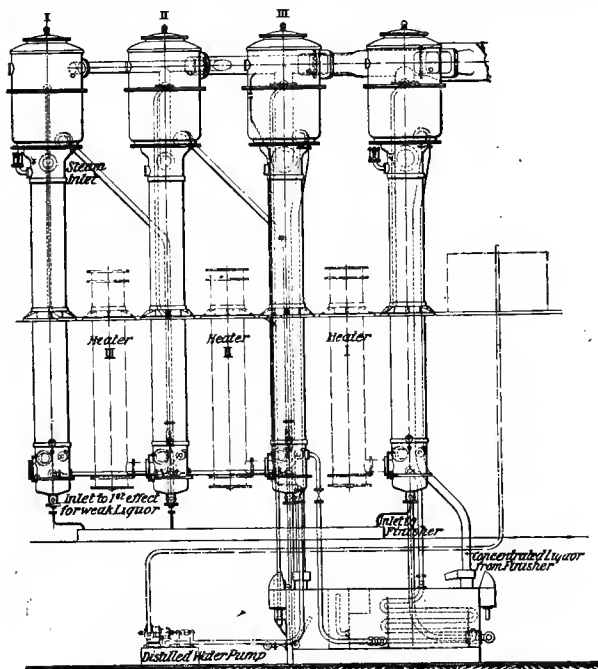
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THE SALT & ALKALI INDUSTRY

INCLUDING
POTASSIUM SALTS AND THE STASSFURT
INDUSTRY

BY

GEOFFREY MARTIN, *D.Sc. (Lond.), D.Sc. (Bristol), Ph.D.*
Technological Chemist

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PREFACE

THE present volume forms the sixth of our series of manuals of technological chemistry, and deals with the salt and alkali industry and the Stassfurt industry of magnesium and potassium salts.

These industries are not only among the oldest, but they are also among the largest and most important of all chemical industries.

They form, so to speak, the basis or groundwork on which are erected most of the great trades of industrial countries.

A few instances will make this clear.

The world's annual production of salt amounts to well over the enormous total of 10,000,000 tons. From this salt, as parent substance, there springs the huge industries which are concerned with the manufacture of sodium sulphate, hydrochloric acid, sodium carbonate, caustic soda, chlorine, hydrogen, etc.

Out of these industries in their turn spring the industries concerned with the manufacture of soap, glass, glycerine, dynamite and other nitroglycerine explosives, bleaching powder, chlorates, etc. These products in their turn form the raw materials of great trades, which ramify one into another in a way which it is difficult for the non-technical reader to realise.

For example, a stoppage in our supplies of salt would cripple the house-building trade, because window glass would be unobtainable in quantity, since sodium sulphate or sodium carbonate are used in glass manufacture, and these products are derived from salt.

The production of explosives would suffer, because glycerine (and incidentally soap) would cease to be producible in quantity; and so mining operations would become difficult, and coal would

become dear. The textile and paper trades would be crippled, because bleaching, sizing, cheap soap for scouring, and other necessary chemicals—all derived, ultimately, from salt—would cease to be obtainable in quantity. These trades would react on other trades in a way altogether difficult to foresee.

Such examples could be extended indefinitely, but enough has been said to enable the reader to grasp the fundamental importance of the industries dealt with in this volume.

The first four chapters—namely, those dealing with the manufacture of salt, sodium sulphate, and sodium carbonate by the Leblanc process—were contributed by the Editor.

The section on the manufacture of sodium carbonate by the ammonia soda process was contributed by the well-known expert, Mr Stanley Smith, M.Sc. (Birmingham). The Editor ventures to suggest that this is the most authoritative and detailed account of the process which has been published up to the present time.

The remaining chapters on the Stassfurt industry and on potassium salts are from the pen of Mr F. Milsom, B.Sc., late research chemist to Messrs Hopkin & Williams, of London, and at present chemist to Messrs Harrington Bros., of London. These sections have especial interest at the present time owing to the fundamental need of potassium salts in the agricultural industries, and the shortage of supplies all over the world owing to the stoppage of the German supplies from Stassfurt.

The Editor will be much obliged if practical men will call his attention to any errors or omissions in the present work which have escaped his attention.

GEOFFREY MARTIN.

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CHAPTER I



The Salt Industry

CHAPTER I

THE SALT INDUSTRY

LITERATURE

- FÜRER.—“Salzbergbau und Salinenkunde.” 1900.
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 —“The Manufacture of Salt.” *Products and Machinery*, March 1914, p. 40.
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 WARD.—*Trans. Manchester Geol. Soc.*, 18, 396, 19, Part VII., 1886-1887.
 RIEMANN.—“Monographien über Chemisch-technische Fabrikation-methode,” Band 18.
 Halle, 1909.
 “Home Office Report on Mines and Quarries,” Part III. (annual).
 “Final Report on First Census of Production,” 1907, pp. 56-58, 81-82.

Much curious information regarding salt is given in the following articles in magazines :—

- E. GOLDSMITH.—“Salt-making in the Far West.” *Journ. Franklin Inst.*, 1904, 159, 45.
 S. HARTMANN.—“Salt Meadows.” *Harper’s Monthly Mag.*, 1902, 106, 959.
 A. INKERSLEY.—“Salt Sea in the Desert of Colorado.” *World’s Work*, 1902, 4, 2105.
 PARKER.—“Salt and Gas Wells of China.” *Chambers’s Journ.*, 1896, 73, 545.
 “Salt Formation in Cheshire.” *Cornhill Mag.*, 1892, 66, 256.
 “Salt Region, Cheshire.” S. Baring Gould, *Good Words*, 1893, 34, 59.
 “Salt Works.” *New Eng. Mag.*, New Series, 1909, 41, 489-492.

COMMON salt, sodium chloride (NaCl), is a mineral found in great abundance in nature. Economically the substance is of great importance, for not only is it an essential component of the food of man and animals, but also it is the source whence, industrially, most of our sodium salts are manufactured: for example, it is the raw product for the manufacture of salt cake (sodium sulphate), sodium carbonate, caustic soda, soap, etc. The only exception to this rule is sodium nitrate, which is found native in very large quantities in Chili.

Occurrence of Salt.—Immense deposits in the form of rock salt are found in many parts of the world. The principal deposits occur at Wieliczka, in the Carpathians (where the deposits are said to be 1,200 ft. thick and the mines have been worked since the eleventh century); at Cordan (near Barcelona) in Spain, where there are two hills of very pure rock salt, each about a mile in circumference; at Stassfurt in Germany, where the layers exceed 3,000 ft. in thickness and are first reached at a depth of 832 ft. from the surface. It also occurs in the Alps at Salzburg, Hall, Hallein, Ischl, Aussee, Berchtesgaden, Heilbron, etc., etc.

Very extensive deposits of salt occur in China, Africa, Asia, Mexico, Colombia, Venezuela, and Russia. In fact, the richest deposit of rock salt in the world is said to occur near Iletz Zashtchiti in the province of Orenberg, south-east Russia.

In the United States and Canada very extensive deposits occur, the principal localities being New York State, Michigan and Ontario, Utah, Virginia, Ohio, Louisiana, and Kansas.

The main British deposits occur in Cheshire and Lancashire, while it is also found near Carrickfergus and near Larne in Ireland.

At Northwich, in Cheshire, the top bed of rock salt is 75 ft. thick and lies 135-150 ft. below the surface. Under this comes a layer, 30 ft. thick, of hard marl, and then comes a second bed of rock salt 105 ft. thick. Below this come successive thin beds of salt. At Winsford in Cheshire the beds are similar to those at Northwich, the upper bed of salt being 70 ft. thick and the lower 120 ft. thick. Similar beds occur at Droitwich and Stoke Prior in Worcester, at Preesal in Lancashire, near Barrow-in-Furness, in Staffordshire, and various other localities.

Composition of Rock Salt.—The natural rock salt, as it occurs in the mines, is usually strongly contaminated with calcium sulphate and magnesium salts, and so cannot be directly used. The following figures refer to the average composition of some rock salts which are commonly met with:—

	Cheshire.	Stassfurt, "Jüngere Steinsalz."	Stassfurt (Impure).	Wieliczka (White).	Cardona.
NaCl	98.30	97.0	94.57	100.00	98.55
CaSO ₄	1.65	1.5	0.89	...	0.44
Mg salts	0.05	0.5	0.97	...	0.02
CaCl ₂	0.99
Alumina and ferric oxide	3.35
Water	...	1.0	0.22
Total	100.0	100.0	100.00	100.00	100.00

Sea Salt.—Enormous quantities of salt are found in the oceans and seas, whither it has been brought by the rains and rivers flowing from land to sea, a process which has gone on without interruption for millions of years, and is still continuing. The sea water evaporates, falls as rain on the land, and runs back into the sea by means of numerous rivers and rivulets. Thus the salt and soluble components of the soil are being continually washed away from land to sea, and the stores of salt now accumulated in the seas and oceans represent the net result of the lixiviation or extraction of land for many geological ages.

100 g. of sea water contain:—

	The Ocean.	The Mediterranean.	The Dead Sea.
	Grams.	Grams.	Grams.
NaCl	2.723	3.007	8.79
MgCl ₂	0.334	0.385	8.99
MgSO ₄	0.225	0.249	...
CaSO ₄	0.126	0.140	0.14
KCl	0.077	0.086	1.36
MgBr ₂	0.008	0.008	0.37
CaCO ₃	0.012	0.012	2.38
Total salts	3.505	3.887	22.03

To every 100 g. of NaCl in ocean salt we have:—

	Grams.		Grams.
NaCl	100.00	KCl	2.83
MgCl ₂	12.27	MgBr ₂	0.29
MgSO ₄	8.26	CaCO ₃	0.44
CaSO ₄	4.62		

The Dead Sea really consists of mother liquors from which part of the salt has already separated. As regards other seas it may be remarked that the Baltic and the Black Sea are poor in salt, containing only about half the amount of NaCl per 100 g. that the Atlantic Ocean does. It should also be noted that the relative proportions of the salts which occur, for example, in the Atlantic Ocean and the Mediterranean are practically the same, whereas the Caspian Sea is much richer in sulphates. Analogous to the Dead Sea is the Utah Sea, which contains some 20-30 per cent. of salt.

Extraction of Rock Salt.—In many salt mines (especially that at Wieliczka) the salt is systematically mined, by first breaking down the rock salt by means of powder. Then the broken salt is shovelled into trucks and sent to be ground into a more or less fine powder at a crushing and grinding mill placed at the bank of nearly every rock salt pit, when it is ready for shipment.

In order to support the roof, columns of either unchanged rock salt are left at intervals, or else the hollow spaces, from which the salt has been removed, is filled in again with debris.

The pillars which are left to support the roof are in proportion to the depth of the mine. Thus at 330 ft. one pillar is left for every $11\frac{1}{4}$ times its area of salt worked. The pillars are usually 10 yds. square, and are separated by intervals of 25 yds.

However, it is now usual to direct water systematically upon the salt so as to prepare a **saturated solution of brine**. This is then pumped up to the surface, and is either piped directly to alkali works, or to where salt is required in the solid conditions; the brine is evaporated in the manner we will presently describe, and the salt allowed to crystallise out.

In this manner great chambers are hollowed out in the rock salt beds in certain mines, and means have to be taken to prevent the roof from subsiding by leaving undissolved certain pillars of salt or by timbering, etc.

In Cheshire, **natural brine** which penetrates only to the upper bed of salt is reached by sinking a shaft some 10 ft. in diameter lined with cast-iron cylinders jointed together or backed with timber. This shaft is carried down until the marl covering the rock salt (which is fairly impervious to water) is reached. Then a bore-hole is driven in until the natural brine is tapped. The brine rushes up into the shaft often with great force, and is then raised by common pumps to the surface, whence it flows into reservoirs lined with puddle clay and brickwork. Occasionally large wooden tanks are employed as reservoirs, the timbering being held together by wooden plugs (nails cannot be used on account of corrosion). From these reservoirs the brine is piped directly to the salt pans or to alkali works.

The piping used sometimes consists of trunks of trees bored out in the centre and tapered at the ends, so that the end of one pipe fits into that of the next pipe. Iron piping is also used, but is regarded as inferior to wood piping in some respects.

In cases where no natural brine is found a shaft is sunk, in the manner above described, to the layer of rock salt and then a stream of fresh water is pumped down on to the bed of salt, allowed to saturate with salt, and then is pumped up again.

The concentrated brine is heavier than pure water, and so collects at the bottom of the shaft, and care is taken to draw only from the bottom of the shaft, the pumps being only worked so long as the brine comes up almost saturated (since weak brine requires much expensive fuel for evaporating the excess of water).

The specific gravity of the saturated brine is about 1.2. As the brine is pumped away from the bottom of the cavity more water flows in, the cavity becomes larger, and the productive capacity of the shaft becomes greater.

However, the removal by solution of these subterranean beds of salt by the agency of water causes in some districts very serious subsidence of the land above them. In fact it is quite common in brine-pumping districts for pieces of land to sink at the rate of 1 ft. a year.

The water finding its way down to the rock salt beds often runs for miles along its surface, and so an ever-increasing layer of salt is removed. When the water becomes saturated the absorption of the salt ceases, but should the water be pumped up again for manufacturing purposes a fresh supply of water flows in, and so the action goes on from year to year, often with bad subsidence of the overlying land.

Manufacture of Salt from Sea Water—Solar Salt

In countries provided with an abundant supply of sunshine, much salt is obtained by the evaporation of sea water. Such salt is called "Solar" salt (Lat. *sol*, the sun).

The chief countries where the process is worked are France, Portugal, Italy, Dalmatia, the Crimea, the United States, and in countries bordering the Mediterranean Sea and the Atlantic Ocean.

In France, especially, the industry is a well developed one; no less than twenty-five large sea-salt works being in operation; the most important company is known as the "Comp. des Product. chim. d'Alais et de la Camargue," and the most important works are situated at the mouth of the Rhone and in the Giraud district.

The general method of work is as follows:—A piece of flat land lying well below the high-water level, is levelled and surrounded by a bank or wall. The best soil to use is clay, which is easily made water-tight. If the land is not clay the ground is puddled with clay to make it water-tight.

The enclosed space, often many acres in extent, and called a "salt garden" or "salt meadow," is divided into compartments by internal walls. Sea water is now admitted into A (Fig. 1) at high tide (usually in spring), and is allowed to stand in this shallow "concentration" pond until the concentration has risen from 3.5° to 25° Bé., *i.e.*, nearly to the saturation point. There separates out at this stage, clay, calcium carbonate (CaCO_3), gypsum (CaSO_4), etc. The concentrated sea water is now allowed to run into the crystallising pond B (Fig. 1), where the

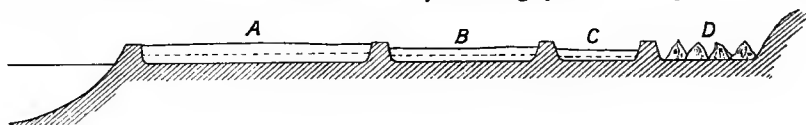


FIG. 1.—Manufacture of Salt from Sea Water.

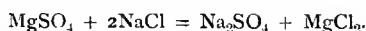
concentration is allowed to proceed until 27° Bé. is reached, when fairly pure NaCl (95-97 per cent.) separates out in a crystalline form.

The mother liquors are now run into other ponds such as C (Fig. 1), and the concentration continued until 32° Bé. is reached, when NaCl of inferior quality is obtained.

The separated salt is then raked together into heaps, and allowed to stand in the air D (Fig. 1); there it slowly dries, the deliquescent salts, such as MgCl_2 , running away or being washed out of the mass by occasional showers.

In good seasons each square metre will produce in forty days some 55-72 kg. of salt.

Now it will be recollected that sea water contains to each 100 g. NaCl present about 12.20 g. MgCl_2 , 8.26 g. MgSO_4 , 4.62 g. CaSO_4 , 2.83 g. KCl, 0.29 g. MgBr_2 , 0.44 g. CaCO_3 . In the course of the evaporation above described, most of the NaCl has been removed, also the CaSO_4 and CaCO_3 . There, therefore, remains behind in the mother liquors much MgCl_2 , MgSO_4 , MgBr_2 , and KCl. In France, in the Giraud district, these mother liquors—now concentrated to $\frac{2}{3}$ of their original bulk—are still worked up, according to a process introduced by Balard, for magnesium and potassium salts, in spite of the development of the Stassfurt deposits (which now supply the bulk of the magnesium and potassium salts of commerce, see p. 83). On further evaporation of these mother liquors we get *sel mixte* crystallising out, a mixture of about 40 per cent. MgSO_4 and 60 per cent. NaCl, and from this Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is made by dissolving the mixture in water and exposing the solution to a natural or artificial cooling a few degrees below 0° C., when the following change occurs:—



The sodium sulphate crystallises out as Glauber salt, while the MgCl_2 remains behind in solution. After the separation of the *sel mixte* there crystallises out Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), which is worked for KCl in the manner described under **The Stassfurt Industry**, p. 83.

In the mother liquors from these residues a considerable amount of bromine occurs, and the liquors are sometimes worked for this in the manner described in Martin's "Industrial Chemistry," Vol. II., under "Bromine."

Recently in the Giraud district in France vacuum evaporating pans have been set up (described below) and a factory for ammonia soda after the Solvay process has also been erected.

In **Russia** (Siberia, N. Russia, etc.) much salt is obtained by allowing sea water to freeze. After removing the ice (which is almost pure water) mother liquors rich in salt are left. These are once more allowed to freeze, the ice removed and, on gentle evaporation, salt separates from the mother liquors. It is purified by exposing to atmospheric moisture. A sample contained NaCl 77.6 per cent.; $MgCl_2$ 1.66 per cent.; $CaCl_2$ 0.94 per cent.; Na_2SO_4 13.60 per cent.; insoluble 6.20 per cent.

Manufacture of Salt from Brine

Much salt is obtained, especially on the Continent, from natural or artificial salt springs which issue naturally from the earth, or are pumped up from below by means of artificial bore-holes (see above). Many of the natural salt springs are almost saturated (e.g., at Lüneberg there is such a spring which has been known since the year 956 A.D.) while others are dilute.

The following figures give the composition of some well-known brines:—

100 Parts Brine Contain	Northwich Bottom Mine.	Droitwich.	Fried- richshall.	Syracuse, New York, U.S.A.	Middles- brough.	Schönbeck.
NaCl	25.790	22.452	25.563	21.710	24.930	9.623
$CaSO_4$	0.450	0.387	0.437	0.505	0.450	0.339
$MgCl_2$	0.093	...	0.005	0.136	...	0.083
KCl, K_2SO_4	0.021
$CaCO_3$	0.018	...	0.010	...	0.030	0.026
$CaCl_2$	0.044	0.188
Na_2SO_4	...	0.390	0.020	0.249
$MgCO_3$...	0.034
$MgSO_4$	0.023	...	0.046	0.012
$FeCO_3$	0.005	...	0.001
Total	26.395	23.263	26.038	22.544	25.476	10.354

In parts of Germany and the Continent, in cases where these salt springs contain less than 16 per cent. of salt, they are sometimes concentrated by allowing the liquor to drip over tall blackthorn hedges in the free air. An enormous surface is thus exposed to the air, and $CaCO_3$, $CaSO_4$, etc., deposits on the thorns and twigs of the wall. However, this process is uneconomical, because much salt is lost by being blown away by the wind, and practically it is found more economical to either buy rock salt and add it to the water from the springs and so bring them to saturation point, or else to penetrate the underlying salt beds by means of bore-holes and allow fresh water to run down and saturate itself with salt. This brine is then pumped up.

The brine, brought up to the saturation point, is next run into large "salt pans" and boiled down for salt.

These salt pans are made of wrought-iron plates riveted together, like boiler plates, and heated from below. At Northwich, the smallest pans employed are 25 ft. long by 20 ft. wide, and $1\frac{1}{4}$ ft. deep, but larger pans used for making coarser salt are 70-140 ft. long by 25-30 ft. wide by $1\frac{1}{2}$ ft. deep. Many salt pans hold over 50 cub. m. of brine. The pans are placed upon brickwork, which forms the flues, while the fireplaces are put in front.

Fig. 2 shows a cross section through a typical English salt pan.

The salt pan A is heated by flues running underneath and, supported upon the flue walls, has running down each side at C C a narrow gangway, made of 2-in. planks, 2 ft. wide, known as the "standing aside." These gangways run the entire length of the pan, and are used by the workmen for shovelling the salt out of the pan on to the "hurdles" D, consisting of wooden planks, inclined as shown, with a gutter placed at the edge. These form a receptacle for the wet salt, the gutter allowing any brine flowing from the wet salt to flow back into the salt pans. As considerable strength is required to shovel out the salt from the pans on to the hurdles, a narrow "toe space" is left beneath the pan, so that the workman in drawing the salt out of the pan can get his toe under the pan and so exert greater force. The pans at the side extend some 6 in. or more beyond the flue walls, in order to give this "toe-room" to the workmen, and also to keep the angle irons at the sides well out of the flues and so prevent them from becoming heated strongly. The pans also extend about 1 ft. to $1\frac{1}{4}$ ft. beyond the iron wall of the fireplace

(in order to prevent the angle irons of the sides becoming unduly heated). The salt is drawn from the pan by a sort of perforated shovel known as a "skimmer."

The plates of the pan which are directly over or near the fires are thicker (e.g., $\frac{3}{8}$ in. thick) and smaller than the other plates ($\frac{1}{8}$ in. thick), because they wear away more rapidly. Each set of fire-plates is separated from the neighbouring series of fire-plates by the long plates resting upon the wall dividing the two fireplaces. The floor of the pan is firmly joined to the sides by means of an angle iron. All the plates are riveted together like boiler plates, and are made out of wrought iron.

A somewhat different arrangement is adopted in Continental salt works. Here

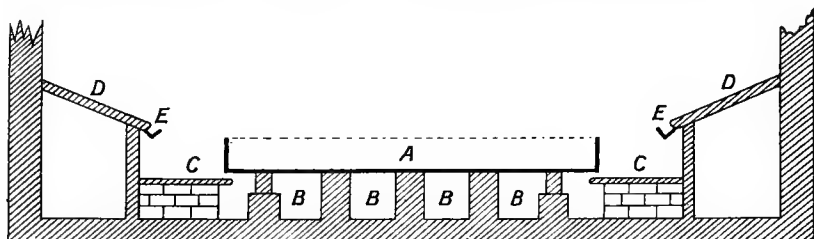


FIG. 2.—English Salt Pan.

the salt pans are usually covered with a wooden cover, provided with an upright shoot to take off the steam. This cover keeps in the heat and accelerates the drying of the salt.

Figs. 3 and 4 show, for example, a typical German salt pan as worked at Schönebeck. The heat is supplied from two fireplaces A and B (using "brown" coal), and the hot gases therefrom stream

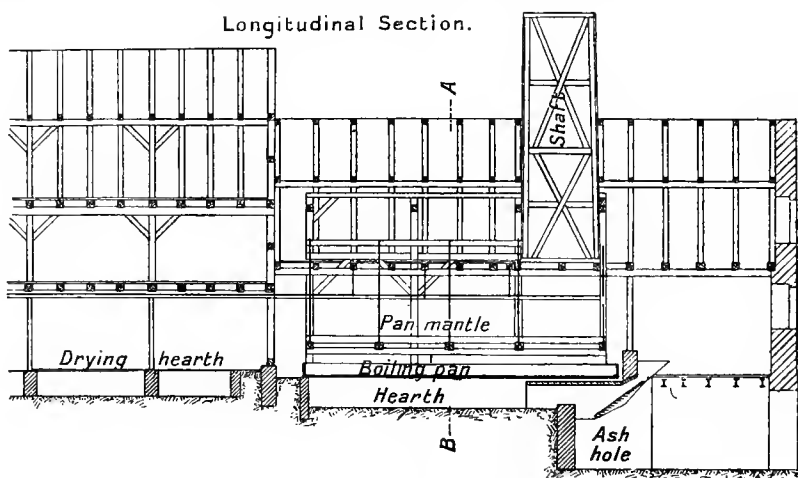


FIG. 3.—German Salt Pan at Schönebeck.

under the pan backwards and forwards several times through flues arranged as shown in Fig. 5, the hot flue gases finally escaping away to the chimney by passing underneath the "drying hearths" which are adjacent to the salt pans as shown. In these drying hearths the salt is finally dried.

The evaporation of the brine is on the Continent usually carried out in two distinct stages.
1. The brine is first run into circular pans provided with stirring gear ("Störpfaunen"), and evaporated until the brine is quite saturated. At the same time a certain amount of purification is effected at this stage, because here there separates (together with some NaCl) such substances as CaSO_4 (gypsum), Na_2SO_4 , Fe(OH)_3 , and certain organic resinous matter (known as "Quellsäure" and "Erdharze").

2. After the brine has been saturated and purified, as above described, it is next run into the salt pans ("Siedepfaunen"), where it is boiled down as described in the English process. Here the salt is separated in a fairly pure form in crystals, and by means of rakes and perforated shovels is

drawn out, placed wet upon a dripping board or mantle ("hurdles") above the pans, so that the uprising steam serves to dry it, and then is transferred, by means of suspended iron trucks, into the drying rooms.

The drying process is completed on iron or stone floors adjoining the salt pans and heated underneath by flues, through which stream the waste hot gases escaping from the salt pan fires (see Fig. 3). This method causes lumps to form in the

Section through A.B.

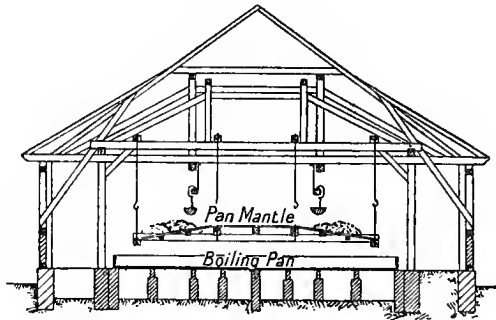


FIG. 4.—German Salt Pan at Schönebeck.

salt, and consequently the better qualities of salt are often slowly dried on wooden gratings or in perforated shelves in special drying chambers.

The varieties of salt formed differ considerably according to the temperature at which the pans are worked.

Fine-Grained or Lump Salt is made by actually boiling the brine in small-

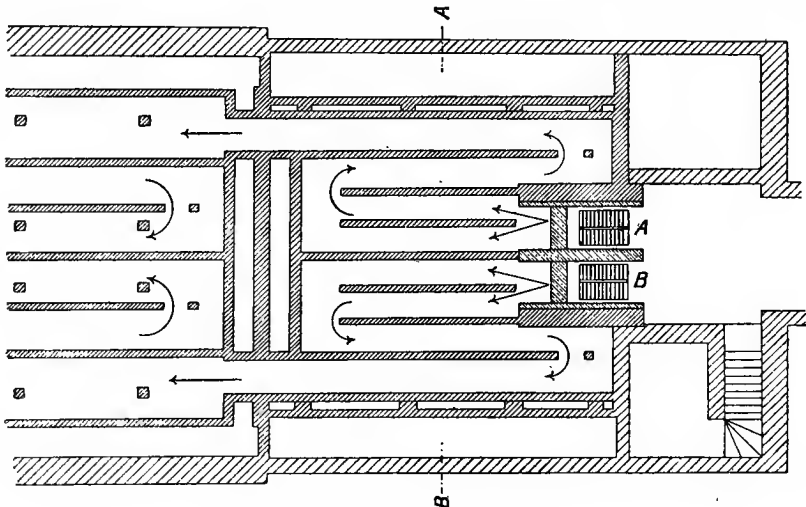


FIG. 5.—German Salt Pan at Schönebeck.

sized pans (say 20-40 ft. long by 20-25 ft. wide and 16-18 in. deep). The temperature of the boiling brine is 107.5°C. , and the salt as it settles out is raked off the fire-plates to the side of the pan. Every eight to twelve hours the salt is withdrawn from the pan and placed in wooden boxes. On cooling, the hot brine still contained in the salt crystallises out and knits the whole into a solid lump, which is then knocked out of the box and dried in a drying chamber.

Table salts are prepared from this fine-grained lump salt simply by grinding.

The best varieties of **German table salt** are prepared by removing salt wet from the pans, allowing to drain on dripping boards, then throwing into centrifugal machines, which force out the excess of moisture. The final drying then takes place in horizontally placed rotating copper cylinders, coated internally with cement (since copper and even tinned copper are attacked by moist salt) and provided internally with a rotating worm, which keeps turning the salt over. Hot air is passed in a steady stream through the cylinder, whereby the salt is dried without the formation of "lumps." It then possesses a brilliant white crystalline appearance.

The following analyses give the average composition of three typical specimens of table salt, to which is appended a specimen of salt derived from sea water :—

	Table Salt from Brine.		Sea Salt.
NaCl	98.40	97.40	97.11
CaSO ₄	1.30	0.58	1.10
MgSO ₄	...	0.15	0.23
MgCl ₂	0.28	0.08	0.04
Insoluble residue	0.03	...	0.05
H ₂ O	...	1.71	1.40
	100.01	99.92	99.93

Magnesium chloride (MgCl₂), if present in salt to any extent, causes an intensification of the salty taste, but, being hygroscopic, causes the salt to become lumpy and damp. It should, however, be noted that even the purest samples of NaCl have a tendency to stick together in lumps. In some table salts this difficulty is got over by adding a small amount of bone meal (calcium phosphates) to the salt. Thus **Cerebros** salt is stated in a recent lawsuit to contain 3 per cent. of phosphates thus added, which possibly acts beneficially in adding mineral phosphates to the food in small quantities.

For "**Common Salt**"—as used in certain manufacturing operations—the crystallisation of the salt is effected at 60°-80° C. in large pans, 40 ft. by 25 ft. by 1½ ft. The salt is raked from the fire-plates every two hours and taken out of the pan every twenty-four to forty-eight hours, and, after draining on the hurdles, is ready for shipment. The grain of this salt is much coarser than the previous variety mentioned.

Fishing Salt, made for the fishing industry, is a coarse-grained variety made by crystallising at 38°-60° C. in large pans, often 60 ft. long, 2 ft. deep and 25 ft. wide. The salt is removed every seven to fourteen days. The longer the salt remains in the pans the coarser the grain. A little alum added to the brine favours the formation of large hard crystals.

Bay Salt is still coarser in grain than fishing salt, the pans being very large, sometimes 135-140 ft. long by 30 ft. wide and 2 ft. deep. The brine is kept at 40°-50° C. and the salt is drawn from the pan every three or four weeks.

The grain of salt can be altered to some extent by adding various substances to the pan. *E.g.*, **Alum** favours the formation of large crystals (*i.e.*, a coarse-grained salt) while gelatine or grease tends to cause a fine-grained salt to be deposited.

"**Hopper**" Salt is made by adding alum to the salt, when the salt crystallises out in hollow cubes, which float about before they sink to the bottom of the pan.

Various impurities gradually separate out on the pan—mostly over the fire-plates—and form a scale over the bed of the pan. Thus any bicarbonate of calcium (CaCO₃.H₂CO₃) is decomposed and a layer of CaCO₃ is deposited (CaCO₃.H₂CO₃ = CaCO₃ + CO₂ + H₂O), forming what is known as "sand scale." This has to be broken occasionally by a hammer or blunt pick and is removed, otherwise the fire-plates would get red hot and burn away.

Likewise CaSO₄ (Gypsum, calcium sulphate) present in the brine also settles out as a hard crust, often containing much NaCl, and is known as "pan scale." This latter often attains 4 in. or more in thickness, and is broken out and sold as a "salt lick" for cattle, also for manuring purposes. If the brine contains much MgCl₂ (Magnesium chloride) the preparation of salt occasions difficulties owing to the deposition of scale and other impurities.

Owing to the gradual deposition of scale, and loss of efficiency therefrom, periodically all the liquid is run away and the pan cleaned and scale removed ("picking" the pan).

The mother liquors remaining after the removal of the salt are usually run to waste.

Manufacture of Salt by Multiple Effect Vacuum Evaporators

The introduction of vacuum apparatus for evaporating the brine is of recent date, and triple effect vacuum evaporating pans have now been employed with success for many years at several large salt works.

Multiple effect vacuum pans have been described in Martin's "Industrial Chemistry," Vol. I., 65, under **Soap** (pp. 123-124), under **Sugar** (pp. 155-160), and in Vol. II. under **Chlorine Industry**, and we will not again describe them in detail here except to mention that heat is applied to the vessels through tubes to the first vessel of the series—such heat may be waste steam or hot flue gasses, and is passed through hot tubes immersed in the brine.

The steam generated from the boiling brine in the first vessel is then used for boiling the brine in the second, and the steam from the second heats the third. A vacuum is maintained by a special pump attached to the last vessel, and consequently the last vessel is under the highest vacuum (so the boiling takes place here at the lowest temperature), while in each of the preceding vessels the pressure is greater and so the boiling takes place at successively higher temperatures; so that while

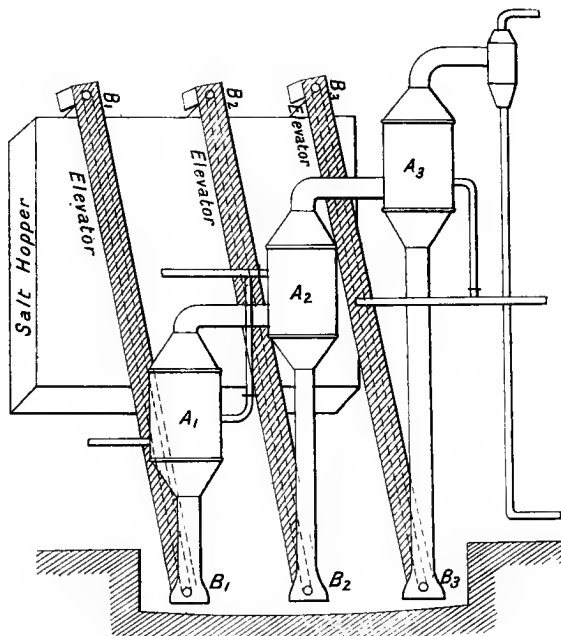


FIG. 6.—Vacuum Evaporators for Salt.

in the first evaporator the pressure may be only a little under atmospheric pressure, in the last evaporator, where a high vacuum is maintained, the boiling takes place at a low temperature.

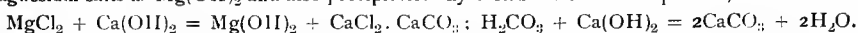
In the vacuum plant designed for salt works special arrangements are made for automatically and continually removing the salt as it separates. Such devices have been described in Martin's "Industrial Chemistry," Vol. I. (Organic), under **Soap**, in describing Foster's salt recovery plant for evaporating soap lies. (See Vol. I., p. 123, and also under "Electrolytic Production of Caustic Soda," Vol. II.) In evaporators employed in salt works, however, very often a long leg is fitted to each evaporator so as to maintain a column of brine equal to the vacuum in the vessel, so that the crystals of salt as they separate out fall into the bottom of this leg and are continually removed by means of an elevator to a storage hopper, and this without in any way interfering with the vacua. Fig. 6 illustrates this arrangement, where each evaporator (A₁, A₂, and A₃) is placed at a different height so as to give a length of leg proportional to the vacuum in the vessel, the evaporator A₃ next the vacuum pump being thus placed at the greatest height. Each evaporator has its own elevator (B₁B₁ belongs to A₁, B₂B₂ to A₂, and B₃B₃ to A₃) for raising the salt as it falls to the bottom of the leg into the hopper.

The earlier attempts to use vacuum apparatus for evaporating brine failed on account of the deposition of calcium sulphate, calcium carbonate, etc., in the form of hard crusts on the internal pipes, which speedily rendered the plant

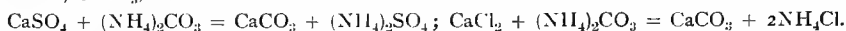
ineffective. Now almost all natural brines are practically saturated with CaSO_4 , which is more soluble in NaCl solution than in pure water, although its solubility is much diminished if either CaCl_2 or Na_2SO_4 or MgSO_4 is present.

Hence many works purify the brine artificially before evaporating in the vacuum pans for salt.

Thus at Lüneburg the brine is treated with some milk of lime, which precipitates the magnesium salts as $\text{Mg}(\text{OH})_2$ and also precipitates any calcium bicarbonate present, thus:—



Next some ammonium carbonate liquors are added, which precipitate all the calcium present, as carbonate, CaCO_3 , thus:—



The precipitated CaCO_3 is allowed to settle and the purified brine thus obtained is run directly into triple effect evaporating pans and boiled down. The salt is automatically recovered (see under **Soap**, Martin's "Industrial Chemistry," Vol. I.) as the evaporation proceeds, and the mother liquor remaining after the removal of as much salt as possible contains all the added ammonium salts either as ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ or as ammonium chloride (NH_4Cl) . This is recovered by adding each time to the liquor excess of lime, $\text{Ca}(\text{OH})_2$, which then sets free the ammonia, and then CO_2 gas is passed into the ammoniacal solution, converting the free ammonia once more into ammonium carbonate, which is once more used for purifying a fresh lot of brine. Consequently for each purification the only chemical which has to be added each time is lime, the ammonia being used over and over again.

Another successful method of treating the brine is the addition of calcium chloride (CaCl_2) (Vis, 1896), which precipitates the CaSO_4 (by lowering its solubility) in the form of small crystals, which mixes with the salt and does not allow the formation of scale in the tube. The salt, after separation, is washed free from CaCl_2 by means of fresh brine, and the washings are sent with the brine into the evaporators once more, so that the same CaCl_2 is used over and over again.

In 1900 Vis proposed to electrolyse brine until the NaOH formed is sufficient to precipitate the Ca and Mg salts. Afterwards CO_2 gas (flue gases) is passed in to precipitate the rest of salts in solution. A very similar proposal was made by Malcolm and Munton in 1908.

Mechanical devices for stopping the formation of scale in the tubes of the evaporator have also been successful to some extent, e.g., Trump's device (patented in 1908) of placing a circulating pump in the vacuum apparatus, which caused the crystals and mother liquors to be continually returned to the evaporator, thereby favouring the formation of large crystals, which by their scouring action prevented the formation of scale in the tubes.

The salt separated by vacuum evaporator invariably comes down as fine-grained white crystals. It is thrown into centrifugals, and is finally drained as above described. It is almost chemically pure, often containing as much as 99.8 per cent. NaCl .

The grain of salt produced by these vacuum evaporators is always fine, and where a coarse-grained salt is required (essential in certain manufactures), the concentrated brine from the evaporators is allowed to flow into an ordinary open pan where the crystals of salt form slowly and grow to a large size. These tanks are sometimes known as "grainers."

The yield of these vacuum pans is far greater than that of the open pans per ton of fuel burnt.

Thus with an ordinary open pan 1 ton of coal (slack, with 15.20 per cent. ash) will make at most 2 tons of salt, whereas a good triple effect vacuum evaporator will give 5.6 tons of salt for the same amount of fuel burnt. Since the price of fuel is a heavy item in the preparation of salt, any saving in this greatly increases the margin of profit.

Another advantage about the employment of vacuum pans is that their productive capacity is far greater than that of the open pans.

Thus from an ordinary open pan 15.20 tons of salt per twenty-four hours is considered a good yield. However, multiple effect evaporators are built which will produce with ease some 500-700 tons of salt per day.

The main disadvantages of vacuum evaporators are the heavy initial cost, and the care with which the brine is to be purified in order to prevent the covering of the tubes with calcium sulphate scale.

An interesting development of the salt industry has recently taken place. The problem of utilising rock salt for the direct production of white salt suitable for commerce and edible purposes, instead of making it from brine, has long occupied the attention of inventors.

This will be obvious when it is recollected that one imperial gallon of saturated brine will only yield on evaporation some 50 ounces of dry salt. Thus there is a great fuel consumption necessary for the evaporation of brine to dry salt. "Fine" salt from brine requires with open pans 13 cwt. of coal, while "common salt" about 9 cwt. of coal, for each ton of salt produced.

Now ordinary rock salt contains clay, gypsum, and is stained by iron and metallic oxides all sorts of colours, ranging from brick red to green or violet. Hence, in order to produce a commercial salt of good quality direct from rock salt we must remove all traces of these staining impurities. Now the temperature at which salt fuses, viz., 776°C. , is so much lower than the very high fusion temperature of the impurities contained therein, that it is possible to purify it by fusion alone. A great many attempts have been made to purify by fusion, but until very recently with no commercial success. It is stated that Lee, working for the International Salt Co., whose works were at Carrickfergus in Ireland, has overcome these difficulties, and that the process may in time revolutionise the salt industry. Lee found that when salt is melted in an ordinary crucible, and agitated by a stream of air, and then is maintained molten for a considerable time, the impurities settle out at the bottom, sinking through the molten salt. On cooling, the whole of the earthy impurities deposit at the bottom in distinct laminæ, the separation showing a straight well-defined line, the bulk above it being pure white salt of a good appearance.

Lee next carried out these laboratory experiments on the large scale. The crude rock salt was melted in a furnace of the same type as an open hearth steel furnace, and was then run into large vessels, termed "converters," into which air was blown. The salt, on cooling, shrank away from the walls, and gave a similar line of demarcation between the pure salt and the impurities, as had been obtained on the small scale. However, very great practical difficulties were encountered. The clayey matter became viscid, and formed a clog upon the bed of the furnace, which prevented the free running of the salt into the converter, and caused much salt to remain behind mixed with clay.

The yield of pure salt thus obtained made the process hopeless as a commercial venture. Consequently, it was found necessary to depart altogether from the type of an ordinary metallurgical furnace. The furnace employed had an internal platform, upon which crushed rock salt was discharged at various openings, and accumulated along the platform in the form of cones. When these cones of rock salt melted under the heat of the furnace, the melted salt flowed away, leaving a residue of clayey matter, etc., capable of being easily removed. The molten salt was now allowed to run down to the bed of the furnace, and when enough of the molten fluid had accumulated, air was blown through the salt in the furnace itself, thus doing away with the use of converters. The molten salt was now allowed to stand some time to allow the impurities to deposit, and was then run into moulds, where it was quickly cooled. The salt was then transferred to crushing and grading machinery, where it was graded into the different kinds of finished salt.

Lee estimates that ^{there} 1 ton of coal will by this process give 12 tons of purified finished salt. Exclusive of the price of rock salt, the price of its conversion into pure grade commercial salt, including depreciation on apparatus, does not exceed 2s. 6d. per ton.

There is, it is claimed, much saving of labour as well as a quick turnover on capital invested by this Lee process than by the usual brine process. Whether the process will stand the test of time and the introduction of vacuum pans into the salt industry by the brine process remains, however, to be seen.

The first patent was taken out by Lee in 1903, and several additional patents have since been taken out for improvement in the process.

Properties of Salt.—Sodium chloride crystallises in cubes of sp. gr. 2.2, and hardness 2. The following figures give the solubility of salt in water at various temperatures:—

THE SALT INDUSTRY

Temperature.	NaCl in 100 g. Solution.	NaCl taken up by 100 g. Water.
0° C.	26.3	35.7
10° „	26.4	35.8
20° „	26.4	35.9
50° „	26.9	36.8
100° „	28.1	39.1
107.7° „	28.4	39.7

The following figures give the specific gravities of salt solutions of various strengths at 15° C. :—

NaCl per 100 g. solution	5 g.	10 g.	15 g.	20 g.	25 g.	26.8 g.
Specific gravity	1.0355	1.0726	1.1105	1.1497	1.1904	1.2055

Statistical.—The manufacture of salt is carried out in Great Britain in forty-eight registered “works.” Of these, ten occur in the North of England, twenty-eight in Cheshire, North Wales and Lancashire. (See “Forty-Ninth Annual Report of Alkali, etc., Works,” 1913, p. 5.)

The total quantity of rock salt mined, white salt made from brine, and salt contained in brine used for making alkali, amounted in 1907 to 1,979,000 tons, valued at £644,000, and this quantity has remained fairly constant for many years past. (See “Home Office Report on Mines and Quarries for 1907,” Part III., Cd. 4343.)

The “Final Report on the First Census of Production of the United Kingdom” (1907) states, p. 56, that the total output of salt works in 1907 was :—

	Quantity.	Value.
	Tons.	£
Rock and white salt	1,417,000	618,000
Table salt (sold in jars or packets)	35,000	77,000
Other products	...	17,000
Total of salt	1,452,000	712,000

The difference between these latter returns and the total amount mined is due to the fact that alkali manufacturers pump large quantities of brine directly in their works and the amount used by alkali manufacturers is not included in this latter estimate.

The amount of salt of different qualities produced may be estimated from the fact that out of 1,144,000 tons of white salt produced by certain firms in 1907 it was ascertained that :—

277,000 tons	were <i>coarse</i> ,	for chemical and manufacturing purposes.
482,000 „	„ <i>coarse</i> ,	for other purposes.
258,000 „	„ <i>fine</i> .	
127,000 „	„ fishery.	

Total, 1,144,000 tons of white salt.

The price of salt at the works was, in 1907, 8s. 10d. per ton, while the average value of exported salt in the same year on shipboard was 15s. 6d. per ton. The total number of persons employed in Great Britain in salt mines, brine pits, and salt works was in 1907, 4,736 (of which 439 were women); the net output per person employed was £67.

The amount of salt consumed per head of population is 30 kg. = 67 lbs.—due largely to consumption in the alkali industries.

The following figures show the British imports and exports of **white and rock salt** :—

	1907.	1910.	1913.
Exports	582,000 tons (£452,000)	562,000 tons (£465,000)	
Imports	30,000 „ (£23,000)	32,000 „ (£23,000)	

Germany in 1908 produced at twenty-three salt mines and sixty-two brine pits :—

1,164,100	tons rock salt.
648,100	„ refined salt (siedesalz).
29,200	„ salt residues (abfallsalz).

Total, 1,841,400 tons salt.

In the same year there was pumped some 15 million hectolitres of brine.

In the same year she used :—

488,600	tons table salt (7.7 kilos per head of population).
529,500	„ for soda, sodium sulphate (to this must be added brine for the ammonia-soda process).
262,100	„ for other chemical and technical purposes.
49,500	„ for manuring purposes.

Total, 1,445,100 tons (22.8 kg. per head of population).

At Stassfurt 100 kilos rock salt cost 0.45 mark, refined salt 2.8 marks. On table salt is a duty of 12 marks per 100 kilos. As sold in trade, table salt in Germany costs 0.2 mark per kilo (1908).

The salt tax (only on table salt) in Germany produced, in 1908, 58,200,000 marks. Salt for industrial purposes and for cattle are tax free, provided they are denatured. The denaturing agents for cattle salt are $\frac{1}{4}$ per cent. iron oxide and $\frac{1}{4}$ per cent. wormwood powder. For salt to be used in the alkali industry the denaturing agents are 1 to 8 per cent. sulphuric acid or $2\frac{1}{2}$ per cent. sodium sulphate or 8 per cent. ammonia, according to the use to which the salt is to be put.

The salt production of other lands is estimated (1908) as follows : United States, 3,000,000 tons ; Russia, 1,800,000 tons (of which half is produced from sea water) ; France, 1,200,000 tons (of which 40 per cent. is sea salt) ; Austria, 340,000 tons and 7,400,000 hectolitres brine.

CHAPTER II

The Manufacture of Hydrochloric Acid

CHAPTER II

THE MANUFACTURE OF HYDROCHLORIC ACID

LITERATURE

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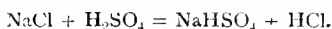
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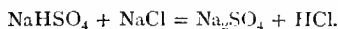
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Manufacture of Hydrochloric Acid.—Hydrochloric acid is usually manufactured by heating two molecular proportions of salt with one molecular proportion of concentrated sulphuric acid. Usually about half a ton of salt is placed in a large semispherical pan set in brickwork and heated by direct firing. An equal weight of concentrated sulphuric acid (1.7 sp. gr.) is added from a leaden cistern, when the following action takes place:—



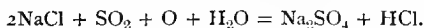
About 70 per cent. of the hydrochloric acid escapes through a flue in the dome of brickwork which covers the pan, and is condensed by water as is described below. The fused mass is finally raked into another part of the furnace, and is there heated to redness, when the action is carried to completeness, thus:—



The hydrochloric acid escapes through a separate flue. This is known as the **Salt Cake Process**, and details of the furnaces, etc., are given fully in Chapter III., p. 27.

The main product is sodium sulphate, the hydrochloric acid being more or less a by-product.

The second process of manufacturing hydrochloric acid is known as **Hargreave's Process**, and consists in passing a mixture of sulphur dioxide, air, and steam over salt heated to dull redness, when the following action takes place:—



The process is fully described under “Sodium Sulphate” in Chapter III., p. 30.

The hydrochloric acid gas evolved in the manufacture of sodium sulphate, either by the salt cake process or the Hargreave's process, is always absorbed by being led into water.

At one time the acid fumes from the salt cake furnaces were allowed to escape into the air. In spite of enormous chimneys reaching to the height of 450 ft. and more, the neighbourhood of the salt cake factories was surrounded by dense clouds of smoke. The acid vapours in the air killed the vegetation for miles around the factories, and brought great distress to farmers. Consequently, in 1863 the Alkali Act was passed which makes it compulsory for 95 per cent. of the escaping acid gases to be condensed. The exit gases should not contain more than 0.2 grain HCl per cubic foot, and the total amount of acid gases escaping must be less than is equivalent to 4 grains of SO_3 per cubic foot.

This at first caused great expense to the factories, as at that time HCl was an almost worthless by-product; but soon the rise in value of HCl for the manufacture of chlorine and bleaching powder made the forcible condensation process an actual source of gain, and at the present time it is common for 99.27 per cent. of the HCl to be condensed.

Fig. 7 shows a typical plant attached to salt cake furnaces, giving 4,800 kg. of sodium sulphate per twenty-four hours. The HCl gas escapes from the salt cake furnaces A, A_1 by means of two separate pipes. One pipe B , made out of acid-

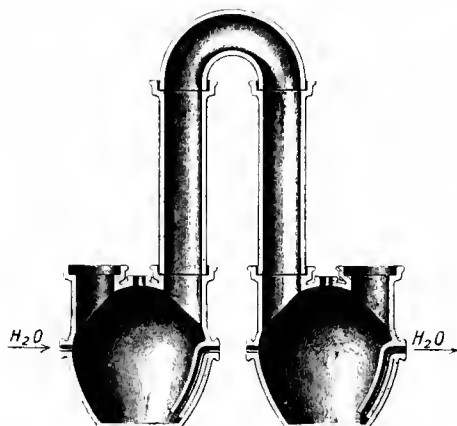


FIG. 8.—Hydrochloric Acid Receivers.

proof earthenware, leads the concentrated and fairly cool HCl gas out of the "pan" in A ; while the other pipe B_1 leads the hot dilute HCl gas out of the muffle or roasting part of the furnace. This HCl gas is dilute and very hot, and so the first part of the pipe B_1 is made of tarred sandstone. The gases pass into two sandstone towers C, C_1 where they receive a preliminary cooling, and are to a great extent freed from dust and sulphuric acid. They then pass through a series of some 50 to 60 acid "receivers." These are simply large "Woulff's bottles," made of acid-proof

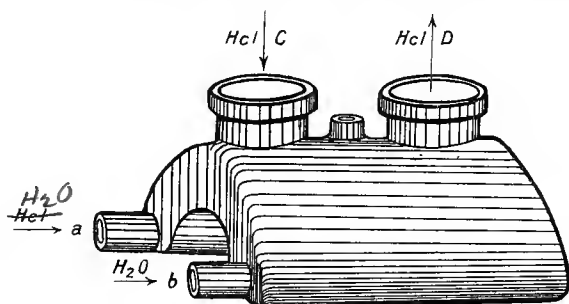


FIG. 9.—Cellarius Receivers.

stoneware, about $32\text{--}37\frac{1}{2}$ in. high, connected together by wide Ω -shaped pipes, and arranged as shown in two parallel rows. They are laid down so that a gentle inclination on slope towards the furnaces exists, so that a stream of water can flow through the series in a direction opposite to that of the gases coming from the furnace. The holes for the water are well seen in Fig. 8. This water absorbs most of the HCl , and is run off into the side receivers G, G_1 .

In Germany the more efficient **Cellarius** receivers have come into use of late years.

Fig. 9 shows a typical cellarius receiver. The gas enters at *c* and escapes at *d*, while the absorbing water enters by the pipe *a*, flows over the "saddle" and escapes by the pipe *b*. Thus a much larger absorption surface is presented to the entering gas, and the latter is more thoroughly mixed with the water and cooled. The whole vessel is immersed in tanks filled with cold water which thus greatly increases the efficiency of the absorption and the strength of acid produced.

The gases finally escaping from the terminal receivers now pass into absorption towers *E*, *E*₁, where they meet a stream of descending water which removes the last traces of acid from the gas.

An absorption tower of improved construction is shown in Fig. 7. It consists of a series of rings of hard earthenware, about 1 m. in diameter, set one on the other so as to form a tower some 15-30 m. high. The upper part of the tower is filled with coke, and the lower part with stoneware plates or bricks. From the water tank *H* a stream of water is sprinkled by means of a rotating "sparger" over the coke and flows in a steady stream down the tower, escaping at the bottom into the stoneware receivers described above.

The gas from the receivers enters at *J* (Fig. 7) at the bottom of the tower, and escapes at *K* into a long earthenware tube *FF*₁ which leads the now acid-free gas away to the chimney. At *L* samples of the acid can be withdrawn and tested.

In England in many works it is the custom to pass the gases evolved from the salt cake furnaces directly into the absorption towers without the introduction of the elaborate system of cooling and absorption vessels described above. These condensing towers are some 20-30 m. high, and are filled with coke or bricks down which a stream of water trickles as previously described. They are usually built of sandstone plates previously boiled in tar or asphalt, made air and water tight with a lute made of tar and clay, and securely bolted together by means of iron clamps and bars. The aqueous acid thus obtained is not quite so strong as that obtained with the more elaborate condensing system, because the gases enter the tower while still hot. The acid, too, is more impure, being contaminated with organic matter, sulphur dioxide, sulphuric acid, chlorine, chlorides of iron and arsenic—the latter substances sometimes being present in considerable quantities, being derived from the pyrites used in making the sulphuric acid used. Within recent years, acid-resisting materials such as silicon-iron alloys (tantiron, ironac, duriron, etc.), fused silica, acid-proof earthenware, etc., have been widely introduced in constructional details of acid plant.

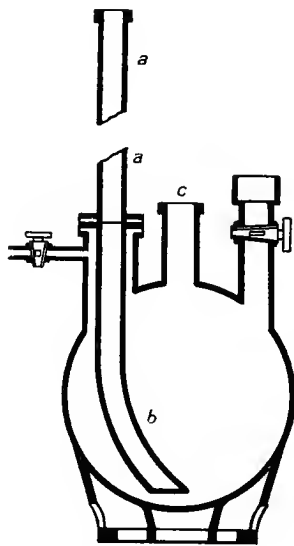


FIG. 10.—Acid "Egg."

The main problem now before hydrochloric acid factories is not so much the condensation of all the *HCl* fumes, but how to condense them in such a manner as to yield **only strong acid** (the only sort saleable), and by the method first described the condensation is now so perfect that it is possible to recover some 99.27 per cent. of the evolved *HCl*, mostly in the form of strong acid of 21° Bé. The strength of the produced aqueous acid depends upon the concentration of the gas and the temperature at which it enters the absorbing water.

For example, a 100 per cent. by volume *HCl* gas at 0° C. gives an aqueous acid containing 45.2 per cent. by weight *HCl*; while a 5 per cent. *HCl* gas under the same conditions will only yield an aqueous acid containing 36 per cent. by weight *HCl* (22° Bé.), and a 10 per cent. *HCl* gas (by volume) will only yield a 39 per cent. by weight *HCl* solution (24° Bé.).

As the temperature of the entering gases increases, so also the strength of the obtainable acid decreases. *E.g.*, a 5 per cent. by volume *HCl* gas at 20° C. will only yield an aqueous acid containing 33 per cent. *HCl* by weight (20° Bé.).

The conditions affecting the condensation of *HCl* have been described at length by F. Hurter (*J. Soc. Chem. Ind.*, 1885, 639; 1887, 707; 1893, 226) and the reader should consult these papers for further information (see also Lasche, *Z. Angew. Chem.* (1894), 6, 610; Lunge, same journal, p. 615).

The problem of the complete condensation of the *HCl* gases evolved in the manufacture of salt cake is first of all complicated by the fact that these gases

contain very variable amounts of HCl. *E.g.*, the HCl gases from Hargreave's and the "open roaster" furnaces may contain much less than 10 per cent. by volume of HCl. Secondly, the cooling down of the gases during the condensing process is rendered difficult by the fact that when the gas dissolves in water it evolves much heat, so that as the cold absorption water is forced against the current of hot gases it rapidly becomes heated, and so does not dissolve the maximum amount possible of HCl. However, the introduction of modern pumps made of stoneware, ebonite, or acid-resisting iron now enables the manufacturers to pump the liquid in a continual stream through the condensing system, and so they can ultimately obtain an acid of 20° Bé. even out of weak HCl gases, such as are evolved from Hargreave's process. The introduction of these acid pumps betokens a great advance on the old system of manufacture.

The acid is best elevated by acid pumps or elevators as described in Martin's "Industrial Chemistry," Vol. II., under **Sulphuric Acid**.

The acid is also elevated sometimes in "emulators," where it is blown mixed with compressed air in the form of a froth from one vessel to another. The old acid "egg" (Fig. 10) still maintains its position as a simple acid elevator but is very wasteful compared with "elevators" and acid pumps. Compressed air forced in at *c* forces the acid contained in the vessel up the tube *ab*.

These "eggs" are sometimes made of strong thick-walled stoneware, which, however, is liable to fracture under a sudden accidental blow.

Casing iron with ebonite is efficient but very costly. Lately there have been placed on the market non-corroding iron alloys such as "tantiron," "ironac," etc., often made of iron mixed with silicon and other components—which are stated to be extremely efficient, as regards their non-corrodibility and their strength. For HCl.aq., however, it is always best to use proper acid pumps for elevating.

Transport and Storage.—The acid is usually transported in large glass "carboys" or in stoneware vessels some 1-1½ m. high. Occasionally ebonite-lined iron vessels or vessels made of guttapercha have been used. HCl is now being transported in railway tank waggons lined with specially prepared waxed wood.

One of the great difficulties of the industry has been the expense of the vessels necessary for storing large quantities of HCl for any length of time, all the more so as more hydrochloric acid is made than is required in industry and so the price is low. The cause of this is the fact that there is a great demand for sodium sulphate, and the accompanying HCl simultaneously produced more than suffices for the demand for the acid.

Where hydrochloric acid is required in places remote from alkali works, it is usually manufactured by the action of sulphuric acid upon salt in special cast-iron cylinders fitted with sandstone doors. This acid is condensed as already described. It is usually much purer than the acid from alkali works and is known in the trade as cylinder acid in contradistinction to "tower" acid which contains more sulphuric acid.

Good commercial cylinder acid should not contain more than 0.5 per cent. of H_2SO_4 .

Purification of the Acid.—The purification of the acid from the various impurities which it contains (*e.g.*, arsenic, sulphuric acid, SO_2 , iron chloride, etc.) is usually carried out in special factories.

Arsenic is detected by means of Marsh's test or by adding stannous chloride, which produces a dark precipitate of arsenic. Arsenic may be removed by adding stannous chloride, settling the precipitate, and redistilling the liquid. Arsenic-free HCl is best obtained by employing arsenic-free materials to start with, but it is often removed technically in great parts by washing the acid with tar oils. **Sulphuric acid** is detected by adding BaCl_2 solution to the dilute acid, when a white precipitate of BaSO_4 is produced if it is present. Sulphuric acid is largely eliminated during the process of condensation, but may be completely removed by adding the proper amount of BaCl_2 and distilling.

Sulphur dioxide, SO_2 , is detected by adding zinc to the diluted acid, when sulphuretted hydrogen, H_2S , is given off and is detected by its blackening effect of lead acetate paper. **Free iodine** is found by adding KI and starch solution to the diluted acid, when a blue colour is produced.

The complete purification of the acid from these impurities is a matter of great difficulty, and where pure acid is essential it is easiest to start with pure sulphuric acid and pure salt, and thus exclude the foreign impurities. When chemically pure HCl is required it is usually distilled in platinum stills.

Technical Uses of Hydrochloric Acid.—In England the main use of concentrated hydrochloric acid is for making chlorine for the manufacture of bleaching powder, chlorates, etc. The acid sold is usually 20°-22° Bé., acids weaker than this scarcely getting a market. In Germany and also in Great Britain large quantities of concentrated hydrochloric acid are absorbed in the colour industry, metallurgical industries, and for very many minor industrial purposes. For example, dilute HCl is largely used for purifying coke, iron ores, clay, for regenerating exhausted animal charcoal, for preparing CO₂ in the aerated water industry, for "pickling" sheet iron in the galvanising industry, so as to remove rust and leave a clean surface for the zinc to adhere to. Also for the manufacture of certain chlorides, in making pottery, and in numerous other things as well. One curious application may be mentioned, viz. the making of freezing mixtures of concentrated HCl and snow, or sodium sulphate.

The acid is also used in analytical chemistry as a solvent, and for titrating purposes. "Aqua regia"—a mixture of HCl and HNO₃—is also made for dissolving gold and making gold chloride, which finds considerable use in photography.

Properties of Aqueous HCl.—The pure concentrated aqueous acid is a colourless liquid fuming strongly in air. One volume of water at 0° absorbs 503 volumes of HCl gas. The following table due to Roscoe and Dittmar (*Journ. Chem. Soc.*, 1860, 128) gives the weight of gas absorbed by 1 g. of water at different temperatures:—

Temperature.	Grams HCl Absorbed by 1 g. H ₂ O.	Temperature.	Grams HCl Absorbed by 1 g. H ₂ O.	Temperature.	Grams HCl Absorbed by 1 g. H ₂ O.
0°	0.825	24°	0.700	44°	0.618
4°	0.804	28°	0.682	48°	0.603
8°	0.783	32°	0.665	52°	0.589
12°	0.762	36°	0.649	56°	0.575
16°	0.742	40°	0.633	60°	0.561
20°	0.721				

When HCl dissolves in water, 17,314 calories are evolved per gram-molecule of HCl dissolved. The composition of the aqueous acid changes when boiled, according to the temperature and pressure employed; but corresponding to a definite pressure a constant boiling mixture of HCl and water is obtained. The aqueous acid which boils unchanged at 110° C. at 760 mm. contains 20.24 per cent. HCl (Roscoe and Dittmar, *loc. cit.*). A weaker solution when evaporated at ordinary pressures concentrates to this strength. A stronger acid loses HCl and also attains this strength when evaporated.

The following table gives the specific gravity of solutions of aqueous hydrochloric acids of given strengths, as given by Lunge and Marchlewski (*Zeit. angew. Chem.*, 1891, 133).

SPECIFIC GRAVITY OF PURE HYDROCHLORIC ACID SOLUTIONS AT 15° C.
(REDUCED IN VACUO), AFTER LUNGE AND MARCHLEWSKI.

Sp. Gr. at 15/4° C.	Degrees Baumé.	Degrees Twaddle.	100 Parts by Weight Correspond to the Following Amount of Pure Acid per Cent.						1 Litre Contains in Kilogrammes.					
			Pure HCl.	18° Bé. Acid.	16° Bé. Acid.	20° Bé. Acid.	21° Bé. Acid.	22° Bé. Acid.	Pure HCl.	Acid of 18° Bé.	Acid of 19° Bé.	Acid of 20° Bé.	Acid of 21° Bé.	Acid of 22° Bé.
1.000	0.0	0.0	0.16	0.57	0.53	0.49	0.47	0.45	0.0016	0.0057	0.0053	0.0049	0.0047	0.0045
1.005	0.7	1	1.15	4.08	3.84	3.58	3.42	3.25	0.012	0.041	0.039	0.036	0.034	0.033
1.010	1.4	2	2.14	7.60	7.14	6.66	6.36	6.04	0.022	0.077	0.072	0.067	0.064	0.061
1.015	2.1	3	3.12	11.08	10.41	9.71	9.27	8.81	0.032	0.113	0.106	0.099	0.094	0.089
1.020	2.7	4	4.13	14.67	13.79	12.86	12.27	11.67	0.042	0.150	0.141	0.131	0.125	0.119
1.025	3.4	5	5.15	18.30	17.19	16.04	15.30	14.55	0.053	0.188	0.176	0.164	0.157	0.149
1.030	4.1	6	6.15	21.85	20.53	19.16	18.27	17.38	0.064	0.225	0.212	0.197	0.188	0.179
1.035	4.7	7	7.15	25.40	23.87	22.27	21.25	20.20	0.074	0.263	0.247	0.231	0.220	0.209
1.040	5.4	8	8.16	28.99	27.24	25.42	24.25	23.06	0.085	0.302	0.283	0.264	0.252	0.240
1.045	6.0	9	9.16	32.55	30.58	28.53	27.22	25.88	0.096	0.340	0.320	0.298	0.284	0.270
1.050	6.7	10	10.17	36.14	33.95	31.68	30.22	28.74	0.107	0.380	0.357	0.333	0.317	0.302
1.055	7.4	11	11.18	39.73	37.33	34.82	33.22	31.59	0.118	0.419	0.394	0.367	0.351	0.333
1.060	8.0	12	12.19	43.32	40.70	37.97	36.23	34.44	0.129	0.459	0.431	0.403	0.384	0.365
1.065	8.7	13	13.19	46.87	44.04	41.09	39.20	37.27	0.141	0.499	0.469	0.438	0.418	0.397
1.070	9.4	14	14.17	50.35	47.31	44.14	42.11	40.04	0.152	0.539	0.506	0.472	0.451	0.428
1.075	10.0	15	15.16	53.87	50.62	47.22	45.05	42.84	0.163	0.579	0.544	0.508	0.484	0.460
1.080	10.6	16	16.15	57.39	53.92	50.31	47.99	45.63	0.174	0.620	0.582	0.543	0.518	0.493
1.085	11.2	17	17.13	60.87	57.19	53.36	50.90	48.40	0.186	0.660	0.621	0.579	0.552	0.523
1.090	11.9	18	18.11	64.35	60.47	56.41	53.82	51.17	0.197	0.701	0.659	0.615	0.587	0.558
1.095	12.4	19	19.06	67.73	63.64	59.37	56.64	53.86	0.209	0.742	0.697	0.650	0.620	0.590
1.100	13.0	20	20.01	71.11	66.81	62.33	59.46	56.54	0.220	0.782	0.735	0.686	0.654	0.622
1.105	13.6	21	20.97	74.52	70.01	65.32	62.32	59.26	0.232	0.823	0.774	0.722	0.689	0.655
1.110	14.2	22	21.92	77.89	73.19	68.28	65.14	61.94	0.243	0.865	0.812	0.758	0.723	0.687
1.115	14.9	23	22.86	81.23	76.32	71.21	68.93	64.60	0.255	0.906	0.851	0.794	0.757	0.719
1.120	15.4	24	23.82	84.62	79.53	74.20	70.79	67.31	0.267	0.948	0.891	0.831	0.793	0.754
1.125	16.0	25	24.78	88.06	82.74	77.19	73.64	70.02	0.278	0.991	0.931	0.868	0.828	0.788
1.130	16.5	26	25.75	91.50	85.97	80.21	76.52	72.76	0.291	1.034	0.972	0.906	0.865	0.822
1.135	17.1	27	26.70	94.88	89.15	83.18	79.34	75.45	0.303	1.077	1.011	0.944	0.901	0.856
1.140	17.7	28	27.66	98.29	92.35	86.17	82.20	78.16	0.315	1.121	1.053	0.982	0.937	0.891
1.1425	18.0	...	28.14	100.00	93.95	87.66	83.62	79.51	0.322	1.143	1.073	1.002	0.955	0.908
1.145	18.3	29	28.61	101.67	95.52	89.13	85.02	80.84	0.328	1.164	1.094	1.021	0.973	0.926
1.150	18.8	30	29.57	105.08	98.72	92.11	87.87	83.55	0.340	1.208	1.135	1.059	1.011	0.961
1.152	19.0	...	29.95	106.43	100.00	93.30	89.01	84.63	0.345	1.225	1.152	1.075	1.025	0.975
1.155	19.3	31	30.55	108.58	102.00	95.17	90.79	86.32	0.353	1.254	1.178	1.099	1.049	0.997
1.160	19.8	32	31.52	112.01	105.24	98.19	93.67	89.07	0.366	1.299	1.221	1.139	1.087	1.033
1.163	20.0	...	32.10	114.07	107.14	100.00	95.39	90.70	0.373	1.326	1.246	1.163	1.109	1.054
1.165	20.3	33	32.49	115.46	108.48	101.21	96.55	91.81	0.379	1.345	1.264	1.179	1.125	1.070
1.170	20.9	34	33.46	118.91	111.71	104.24	99.43	94.55	0.392	1.391	1.307	1.220	1.163	1.106
1.171	21.0	...	33.65	119.58	112.35	104.82	100.00	95.09	0.394	1.400	1.316	1.227	1.171	1.113
1.175	21.4	35	34.42	122.32	114.92	107.22	102.28	97.26	0.404	1.437	1.350	1.260	1.202	1.143
1.180	22.0	36	35.39	125.76	118.16	110.24	105.17	100.00	0.418	1.484	1.394	1.301	1.241	1.180
1.185	22.5	37	36.31	129.03	121.23	113.11	107.90	102.60	0.430	1.529	1.437	1.340	1.279	1.216
1.190	23.0	38	37.23	132.30	124.30	115.98	110.63	105.20	0.443	1.574	1.479	1.380	1.317	1.252
1.195	23.5	39	38.16	135.61	127.41	118.87	113.40	107.83	0.456	1.621	1.523	1.421	1.355	1.289
1.200	24.0	40	39.11	138.98	130.58	121.84	116.22	110.51	0.469	1.667	1.567	1.462	1.395	1.326

CHAPTER III

The Manufacture of Sodium Sulphate (Salt Cake)

CHAPTER III

THE MANUFACTURE OF SODIUM SULPHATE (SALT CAKE)

LITERATURE

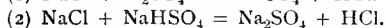
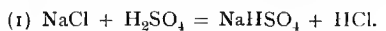
LUNGE.—“Sulphuric Acid and Alkali.” 1913.
T. MEYER.—“Sulfat und Salzsäure.” 1907.

CONSIDERABLE deposits of natural sodium sulphate occur in Persia (near Tiflis), in the Kara-Boghas Gulf of the Caspian Sea, at Tomsk in Siberia, and some other places. Also many inland seas contain considerable amounts in solution, especially the Owens Lake in California, whose waters contain some 11 g. of sodium sulphate per 1,000 c.c.

However, for industrial purposes, the substance is almost always (in Europe at least) obtained from common salt by two main processes; (1) by treating with sulphuric acid (salt cake process), or (2) by the SO_2 , air, and steam (Hargreave's) process.

Small amounts are also obtained as a by-product in the Stassfurt Salt Industry (see p. 83).

1. Salt Cake Process.—The salt used is either broken-up pure rock salt (where this is available), or else salt coarsely crystallised. The sulphuric acid used is usually “Glover” acid, of 58° – 62° Bé. The decomposition occurs in two distinct stages:—



The first reaction begins at ordinary temperatures, whereas the second is only completed at a red heat. The final product is called “salt cake.”

Figs. 11, 12, 13 show the ordinary salt cake muffle furnaces (“blind roasters”) employed.

Figs. 11 and 12 show a vertical and horizontal section through the furnace, while Fig. 13 represents a horizontal section through the lower flues of the furnace. $\frac{1}{2}$ is the large cast-iron “pan,” usually some 3 m. in diameter, some 60 cm. deep, and made some 16–18 mm. thick. It lies with a flange round the edge resting on the stonework of the furnace.

Good iron “pans” will stand several thousand charges before being burnt through. However, they must be composed of cast iron of the proper composition, containing a high percentage of chemically-combined carbon, but only small amounts of uncombined carbon (graphite) and silica, and be of uniform composition throughout (otherwise some parts will corrode more quickly than others).

The vaulted roof of this part of the furnace is built of acid-proof materials, and is provided with an outlet tube $\frac{1}{2}$ of acid-proof earthenware, iron alloy, or fused silica, for the escaping HCl gas.

The salt is introduced into the pan through the opening i_2 (Fig. 12), and the proper amount of sulphuric acid is poured upon it through a leaden tube (not shown), when HCl gas ("pan gas") is at once evolved, and the following action takes place:—



When the evolution of HCl has almost stopped, the iron sliding door k is raised,

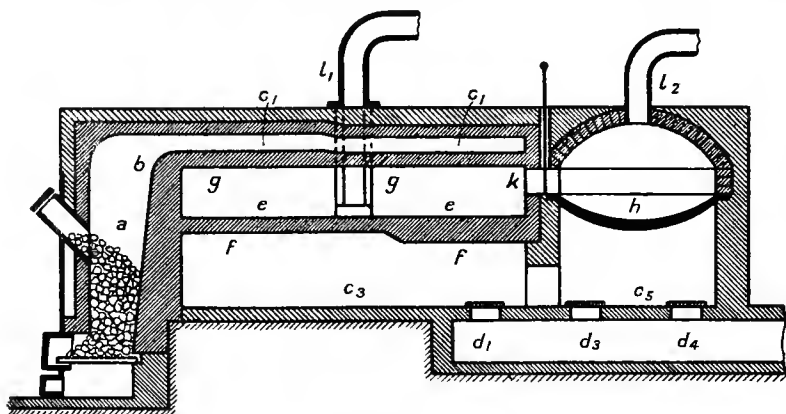


FIG. 11.—Salt Cake Muffle Furnace—Elevation.

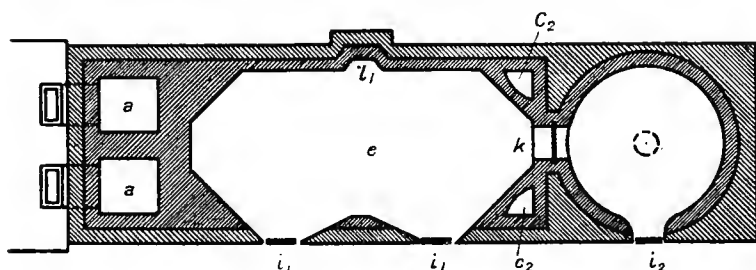


FIG. 12.—Salt Cake Muffle Furnace—Horizontal Section.

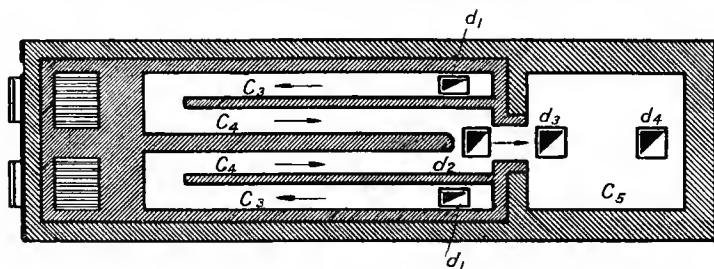
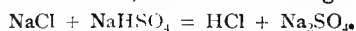


FIG. 13.—Salt Cake Furnace—Horizontal Section through Lower Flues.

and the mass is transferred into the muffle furnace (blind roaster) e , being spread over the floor by means of the doors i_1 . This muffle is composed of fire-clay or other acid-proof material, and is gas-tight although fairly thin walled. In this blind roaster the mass is raised to a high temperature by the hot gases playing round it from the furnace a , and the following change takes place:—



The HCl gas ("roaster gas") escapes through a sandstone pipe l_1 , the HCl gas here escaping being kept separate from the HCl gas (pan gas) coming from the pan through l_2 . The product in the muffle furnace must be constantly raked and stirred. The heating must not be so intense as to cause the finished sulphate to melt, and this regulation of the temperature is secured by allowing the hot gases coming from the two fireplaces *a a* (Fig. 12) to first pass right above the muffle by c_1 , then vertically downwards through $c_2 c_2$, then again horizontally beneath the muffle through $c_3 c_3$, $c_4 c_4$, finally passing by c_5 beneath the pan and heating this somewhat, the gases finally escaping through $d_1 d_1$, d_2 , d_3 and d_4 to the chimney stack.

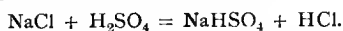
In the early years of the process open hearths were used, in which the flames from the fire played directly on to the mass placed on the hearth. The yield of these "open" roasting furnaces was greater than that of modern muffle (blend roaster) furnaces, and they were also more economical of coal. However, "open hearth" furnaces of this construction have now been almost entirely abandoned on account of the difficulty of condensing the HCl gas (which was thus mixed with the gases from the fire), and the impurities in the gas when condensed were very marked. Moreover, the "condensing" arrangements became choked up with dust from the fires.

The hot product, still emitting HCl gas, is finally raked out into iron transport vessels provided with lids, and standing immediately in front of the furnace. The product called "salt cake" is contaminated with iron, and is usually ground up. Meanwhile a fresh charge of salt is placed in the pan, and the operation repeated.

An average furnace works per day some twelve charges of 500 kg. sodium sulphate or salt cake.

For certain purposes "iron free" sodium sulphate is required—e.g., for making plate and mirror glass—and for this special sulphate the cast-iron pans are replaced by long **lead**en pans, made out of thick-walled lead, rectangular in section, and often some 5-8 sq. m. in area. These are very costly, and unless the firing is carefully adjusted they can be permanently damaged by melting under the heat applied.

Mechanical Salt Cake Furnaces.—Many attempts have been made to carry out the manufacture of salt cake in mechanical furnaces. Mactear's revolving furnace consists of a circular revolving bed covered with a fixed arch, between which and the bed the hot furnace gases stream. A mixture of salt and acid are continually fed into a large basin in the centre of the hearth, where the ingredients mix and react according to the equation:—



The mass overflows into the outer portions of the revolving floor, and are then highly heated by the hot furnace gases. Fixed stirrers continually mix the mass and gradually work it to the circumference over which it drops. The action is thus continuous, and the HCl gas evolved at a constant rate. It is claimed that in spite of the fact that the HCl gas is mixed with the whole of the furnace gases, the condensation is more readily effected and a more concentrated acid obtained than with the ordinary process.

Where mechanical furnaces, however, have not to any great extent displaced the ordinary furnace above described, except in one case—and that is the manufacture of sodium sulphate by heating the acid sodium sulphate (obtained as a by-product in the manufacture of HNO_3 from Chili saltpetre, NaNO_3) with salt, NaCl —the salt and the NaHSO_4 are both ground, and thoroughly mixed in circular flat enclosed ovens, made of special acid-resisting cast iron, and provided with stirring apparatus at the centre. The whole oven is enveloped in the hot gases coming from a furnace, and so the temperature of the whole is maintained at about 700°C . (above this the iron is strongly attacked by the HCl). The stirrers work mechanically with a raking movement from the centre, and continually mix the mass and urge it towards the periphery of the circular floor, where it is rejected as Na_2SO_4 . See Fig. 14.

The HCl gas is evolved in great purity and in a very concentrated form (30-35 per cent. by volume). At Mannheim in 1909 these mechanical furnaces were used to obtain a pure arsenic-free HCl gas, which, after freeing from H_2SO_4 dust in Cellarius condensers, is then led directly into the contact apparatus for Deacon's process for manufacturing chlorine, thereby reducing this latter process to its original simple form (see "Deacon's Process," Martin's "Industrial Chemistry," Vol. II.).

2. Hargreave's Process for Manufacturing Sodium Sulphate.—This process dispenses with the manufacture of sulphuric acid. It depends upon the fact that although pure sulphur dioxide gas (SO_2) of itself does not decompose salt, yet a mixture of SO_2 , air, and steam will in time completely convert salt into Na_2SO_4 . The SO_2 reacts with the NaCl to form a little sulphite, which is then immediately at a temperature of 500°C . oxidised in the presence of air to sulphate, so that ultimately the following equation is realised:—

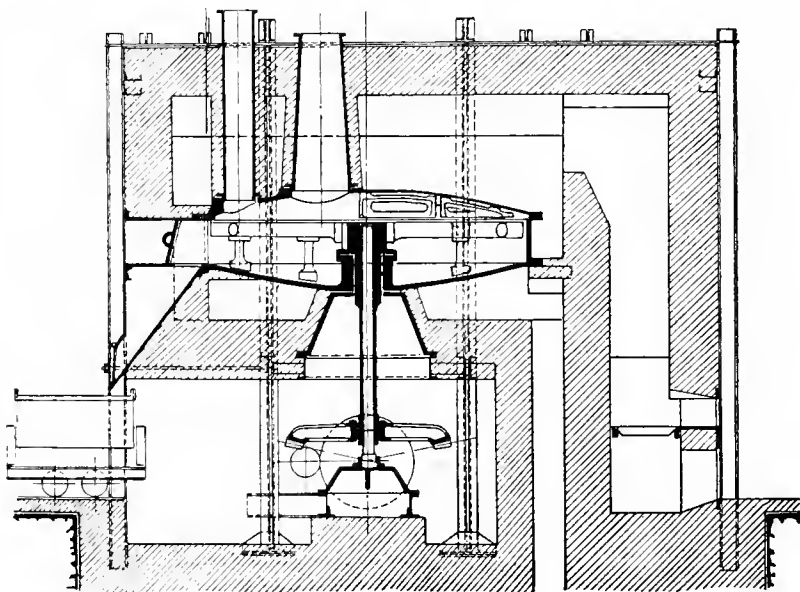


FIG. 14.—Mechanical Salt Cake Furnace.

The hydrochloric acid is separated from the evolved gases by passing them into hydrochloric acid condensing towers.

The salt is moistened and pressed into cakes of about half a brick in size, and then dried so as to form a porous cake. It is then placed in the kilns. These were (and sometimes still are) built of brick, so arranged that each kiln can be put into communication with its neighbour, and each separately heated with a fire. In the best practice, however, some ten large cast-iron cylinders some $5\frac{1}{2}$ m. in diameter by 3.7 m. in height, are connected up in two rows of five cylinders each to form a "cylinder battery." They are then filled with the dry porous cakes of salt, and the hot gases from the pyrites burners (such as are used in chamber sulphuric acid works), mixed with an equal volume of air and some steam, are led into the cylinders from above downwards, the fresh entering gases from the furnaces being led into that cylinder in which the process is most nearly completed (*i.e.*, containing much Na_2SO_4 and little NaCl), while the end gases, from which most of the SO_2 has been absorbed, are led into a cylinder filled with fresh NaCl. In general some eight cylinders are in action at once, the other two being placed out of action for emptying from the formed Na_2SO_4 and refilling with fresh NaCl.

Each cylinder holds about 50 tons of salt, and its complete conversion into sulphate requires about three weeks. The action proceeds best at a temperature of 500°C . Consequently each cylinder is fitted into brickwork and provided with a fireplace so that the whole cylinder can be externally heated. The first and last cylinders of the series are thus heated, but in the intermediate cylinders the action proceeds with the evolution of sufficient heat to maintain them at the proper temperature without the aid of external heat. In fact sometimes cooling of the intermediate cylinders is necessary since if the temperature gets beyond 600°C . the mixture of salt and formed sodium sulphate will fuse and so destroy the efficiency of the cylinder.

Pure salt fuses about 780°C ., pure sodium sulphate at 860°C ., while a mixture of the two at a lower temperature than either component alone, viz., at 600°C .

The gases are drawn off from the last cylinder of the series by means of a porcelain or earthenware exhauster. They contain about 10 per cent. HCl by volume, and after passing through cooling pipes, are led directly into the HCl condensing towers.

It should be noted that according to the equation :—



each volume of SO_2 produces double its volume of HCl gas. A battery, such as that described above, will yield some 7,000-7,500 tons of Na_2SO_4 per year, but the whole process requires very careful adjusting of the temperature, entering gases, etc., etc.

The great disadvantage of the process is the length of time required for the complete conversion of the salt into sulphate.

However, the process has been worked successfully in a great many factories in England since 1872, also in France and Germany.

Properties of Sodium Sulphate.—Anhydrous sodium sulphate (Na_2SO_4) is known as **salt cake**, enormous quantities being yearly produced by one or other of the processes above described. (The annual output is estimated at 360,000 tons.)

Good technical salt cake may contain up to 1 per cent. free H_2SO_4 , 0.1 per cent. Fe, and 0.3-0.5 per cent. NaCl. However, if the substance is to be used for making mirror, plate, and other special kinds of glass, it must not contain more than 0.01-0.02 per cent. of iron, and so must be made from iron-free materials in leaden pans (see above).

In order to purify technical sulphate it is dissolved in water, and after the iron has been precipitated by the addition of calcium carbonate, the solution is evaporated and allowed to crystallise out in the cold, when it separates as "**Glauber's salt**" ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Should the crystallisation be carried out in a boiling solution the sulphate separates out as anhydrous sulphate (Na_2SO_4).

100 parts of water dissolve the following quantities of sodium sulphate, calculated as Na_2SO_4 :—

Temperature	0°	10°	20°	30°	34°	40°	50°	60°	70°	80°	90°	100°	105°
Na_2SO_4 dissolved	5.02	9.00	19.4	40.0	55.0	48.8	46.7	45.3	44.4	43.7	43.1	42.5	42.2

The hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ when in solution passes over into the anhydrous form at about $+32^{\circ}\text{C}$. The solubility increases from 0° to $+32^{\circ}\text{C}$., and thereafter decreases. The saturated solution boils at 103.5°C .

If ordinary Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) be exposed to the air or is heated it loses water and goes into the anhydrous salt.

Heated on charcoal or in the reducing flame, sodium sulphide (Na_2S) is formed (see below).

Sodium hydrogen sulphate, sodium bisulphate, may be prepared by mixing equivalent quantities of Na_2SO_4 and H_2SO_4 , and evaporating at a temperature over 50°C .

Sodium sulphide (Na_2S) is prepared on a large scale by melting sodium sulphate with coal in large "open" roasting furnaces, similar to those formerly used for making sodium sulphate. The hearths are made of "basic" lining, and rapidly attacked by the hot mass. The mass first melts to a thin mobile fluid, and CO gas bursts forth all over the surface and burns. As the heating proceeds, however, the liquid becomes somewhat more viscid. The mass is allowed to cool and the reddish solid is crushed into coarse fragments and lixiviated with water. The clear solution is evaporated, and allowed to crystallise out. The salt comes on the market in deliquescent crystals ($\text{Na}_2\text{S} + 9\text{H}_2\text{O}$), containing some 30-32 per cent. Na_2S . The crystals are sometimes dehydrated and come on the market in a concentrated form, containing some 60-65 per cent. Na_2S . However it is not possible to completely dehydrate the substance.

Sodium sulphide (Na_2S) is used on a large scale for making "sulphur" dyes (see Martin's "Industrial Chemistry," Vol. I.); it is also used in tanneries for removing the hair from skins.

CHAPTER IV

General Survey of the Sodium Carbonate Industry

3

CHAPTER IV

GENERAL SURVEY OF THE SODIUM CARBONATE INDUSTRY

General Survey

Natural Sodium Carbonate is found encrusting the soil in parts of Egypt, being produced, no doubt, by the weathering of the sodium sulphate left by the drying up of old Egyptian lakes and seas.

This sulphate (Na_2SO_4) is reduced to sodium sulphide (Na_2S) by the action of certain fungi and algae. CO_2 in the soil and atmosphere then converts the Na_2S into Na_2CO_3 with evolution of H_2 .

A considerable amount of this natural soda, called "Trona," is even at the present time collected. It has the composition $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + 2\text{H}_2\text{O}$, mixed with salt. Other deposits of natural soda occur in California, Mexico, Persia and other tropical lands, the carbonate actually separating in a crystalline form from numerous tropical "soda" lakes and seas in the dry season, also from the Caspian Sea and the Araxes.

One of the most remarkable deposits of natural soda occurs in the Owen's Lake, California, the waters of which contain per litre 31 g. Na_2CO_3 , 11 g. Na_2SO_4 , and 31 g. NaCl . Some 20,000,000-50,000,000 tons of soda are estimated to be here stored up, and the exploitation of this source has already commenced.

Early in 1911 a company with a capital of £1,312,500 was formed to acquire a ninety-nine years' lease of and to develop the deposit of natural soda covering some 30 sq. miles known as Lake Magadi, in the British East Africa Protectorate, to connect same with the Uganda Railway, about 100 miles, and to build a pier and approaches at or near Kibudini, British East Africa.

The deposit is said to contain some 200×10^6 tons of soda, of which 40×10^6 are in the upper layers.

Refining works are now under construction in Lancashire.

It is proposed to produce some 50,000 tons per annum.

The deposit is remarkably pure. Sodium sulphate is the mother substance of Egyptian soda; however, some deposits of natural soda undoubtedly arise from the decomposition (by atmospheric CO_2) of sodium silicates, silicic acid being set free and sodium carbonate formed.

For many years the ashes of seaweed and of wood formed the chief European sources of potash and soda. But the great demand for cheap soda for making soap for the cotton industry caused Leblanc in 1791, with the assistance of Dizé, to invent the process for converting salt into soda which now bears his name.

The process consists, essentially, in heating salt with sulphuric acid, thereby converting it into sodium sulphate. The sulphate is then ignited with calcium carbonate and coal and is thereby converted into sodium carbonate.

Leblanc, the originator of one of the world's greatest chemical industries, which has given us cheap soap and cheap glass and has poured directly or indirectly untold wealth into numerous lands, did not meet with any reward in his lifetime. He died, by his own hand, a ruined man in the madhouse of a workhouse in 1806; some fifteen years before he had won the prize offered by the French Academy (1791) for the best method of converting salt into soda.

In France political troubles prevented the development of the soda industry. It was Muspratt in England, who in 1824, after the repeal of the salt tax, built the first Leblanc soda factory, and thus created the great chemical industry of to-day. Thus, a supply of cheap sulphuric acid in large quantities is one of the first essentials of the Leblanc process, and so the enormous sulphuric acid industry of to-day owes its origin to the Leblanc process; next, the production of excess of hydrochloric acid, as a waste product, in the salt cake furnaces called into existence the chlorine industry and the manufacture of bleaching powder; so that a group of inter-connected chemical industries sprang up in England soon after 1824, and for more than fifty years English manufacturers and merchants controlled the world's markets. Great soda factories sprang up everywhere in the neighbourhood of the salt and coal deposits, especially at Newcastle-on-Tyne, Glasgow, Widnes, and St Helens in Lancashire.

In 1866 Solvay introduced his "ammonia soda" process, which was the beginning of a new era for chemical industry. No sulphuric acid is necessary in this process for making soda, and no hydrochloric acid is generated; moreover, this process allowed the production of sodium carbonate at much lower cost than the Leblanc process.

Consequently between 1870-1875 the price of sodium carbonate declined from £13 per ton to only £4-£5; and at the present time the Leblanc process is not remunerative, so far as the sodium carbonate is concerned, being mainly kept going by the value of the produced hydrochloric acid (which is required in the bleaching powder industry), the recovered sulphur, and other products.

A new era in the industry began in 1895, when the alkali chlorides began to be electrolysed on the large scale for the manufacture of chlorine and caustic alkalies, and it appears that this new process must gravely threaten the Leblanc process. Indeed the Leblanc process, owing to the competition of these cheaper processes, has ceased to be worked in most countries. Several large Leblanc works are still operated in England, and two in Germany, but it remains doubtful whether they can hold their own in spite of great improvements in plant and process, and the amalgamation of the various interested parties in the "United Alkali Co." We must remember, however, that the Leblanc process works in with the wet copper process, with CS_2 manufacture, and various other important industries. However, the enormous supplies of sodium carbonate formerly consumed by the glass industry have been now largely replaced by the use of the cheaper sodium sulphate. As a consequence of this, the first part of the Leblanc process, namely, the formation of sodium sulphate (salt cake) by the action of sulphuric acid or salt, has actually increased of late years. It is only the second part of the process—the calcining of this sodium sulphate with coal and limestone—that has decreased, subjected as it is to the competitive action of the ammonia soda process.

The ammonia soda process has made rapid headway during the last thirty years, and at the present time it is practically the only sodium carbonate process worked on the large scale in the United States, France, Belgium, and Austria. In Germany it is the main process worked for the production of sodium carbonate, the Leblanc process in Germany being in a very threatened condition, only two factories in 1909 (*viz.*, at Stolberg and at Heinrichshall) now working the Leblanc process.

The ammonia soda process is not threatened to any great extent by the growth of the electrolytic processes for making caustic soda and chlorine, because the amount of sodium carbonate and alkali required for industrial purposes is far greater than the amount of chlorine and bleaching powder required, so that even in the event of the electrolytic processes completely covering the world's demand for chlorine or bleaching powder, the yield of alkali then produced would only be a small fraction of that which is necessary to commerce.

To sum up, it would appear that three main processes will continue to be simultaneously worked on a very large scale, *viz.* :—

1. The **salt cake** process (viz., $\text{NaCl} + \text{H}_2\text{SO}_4$) for making sodium sulphate and hydrochloric acid.
2. The **Hargreave's** process for the same products also seems well established.
3. The **ammonia soda** process for sodium carbonate, sodium bi-carbonate, and caustic soda.
4. The **electrolysis of alkali chlorides** for caustic potash, caustic soda, and chlorine.

On the other hand the calcining of the sodium sulphate with limestone and coal (second stage of Leblanc process) ultimately may be abandoned completely.

Statistics

Counting together the sodium carbonate, bicarbonate and caustic soda, the following figures show the world's production in these chemicals in 1884.

	1884.	
	Leblanc Soda.	Ammonia Soda.
	Tons.	Tons.
England	380,000	52,000
Germany	56,500	44,000
France	70,000	57,000
United States	...	1,100
Austria-Hungary	39,000	1,000
Russia
Belgium	...	8,000
Total	545,500	163,000
	Leblanc Soda.	Ammonia Soda.
Total	708,500	

In 1903 Solvay estimated the world's production of soda as 1,750,000 tons—1,600,000 of which being produced by the ammonia soda process and only 150,000 tons by the Leblanc process.

In 1908 Lepsius put the world's production at 2,000,000 tons, only 100,000 of which being made by the Leblanc process. This quantity shows a consumption of soda of 1.3 kg. per head of population throughout the world.

The German net export, 1909 (after subtracting the slight import), was as follows :—

Soda (principally calcined)	57,400 tons at	90 marks.
Bicarbonate -	1,200	,, 215 ,,
Caustic soda	8,280	,, 215 ,,
Sodium sulphate	65,500	,, 30 ,,
Na_2S and K_2S	7,000	,, 160 ,,

The total value was put at 10,200,000 marks = £510,000.

CHAPTER V

The Manufacture of Sodium Carbonate and Caustic Soda by the Leblanc Process

CHAPTER V

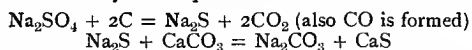
THE MANUFACTURE OF SODIUM CARBONATE AND CAUSTIC SODA BY THE LEBLANC PROCESS

LITERATURE

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 DAMMAR.—“Chemischen Technologie.” 1895. “Chemische Technologie der Neuzeit.” 1910.
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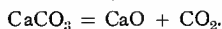
Manufacture of Sodium Carbonate (Soda) and Caustic Soda by Leblanc Process

THIS process consists in melting together sodium sulphate (salt cake), coal, or coke, and limestone or chalk, when the sulphate is reduced by the carbon to sodium sulphide, which then reacts with the calcium carbonate (chalk, limestone) to yield sodium carbonate, as shown by the equations:—

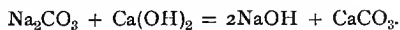


The calcium sulphide (CaS) formed is insoluble in water, so that in order to isolate the sodium carbonate all that is necessary is to lixiviate the mass with water.

In practice a considerable excess of limestone and coal is employed, so that much free CaO (calcium oxide) is formed, thus:—



When this mass is then slaked with water calcium hydroxide is formed with the evolution of heat ($\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2$) which then reacts on the sodium carbonate to produce caustic soda, thus:—



This procedure greatly aids the rapid lixiviation of the mass with water, and indeed at the present time the English Leblanc factories prefer to work the mass solely for caustic soda as it is cheaper and finds a readier sale among soap makers.

Melting Process.—100 parts of sodium sulphate (salt cake), 90-120 of calcium carbonate in the form of limestone or chalk, and 40-80 of carbon in the form of “slack” or powdered coal are heated together in a furnace. It is important that the calcium carbonate should be as pure as possible and that the sodium sulphate (salt cake) should be of good quality.

Fig. 15 shows an old “open” roasting furnace (“black ash furnace”), still fairly widely used. It is provided with two hearths made of fire-fast bricks, embedded with mortar in a layer of stamped clay. The mixture of sulphate, coal, and limestone is first placed on the hearth

A, where it receives a preliminary heating. It is then raked forward to the hotter hearth B, and here heated to bright redness. The mixture first melts to a thin fluid mass, then becomes pasty, and CO_2 gas is copiously evolved. Towards the end of the reaction, little jets of burning CO gas, known as "candles," burst forth over the surface of the fluid mass. During the whole process, a workman continually rakes and mixes the fluid mass by means of long irons inserted through a side door in the furnace; and when the mass reaches the right consistency the charge is withdrawn into iron boxes standing just below the furnace. It requires some experience to know when to withdraw the charge, for if the heating is continued too long, not only is sodium

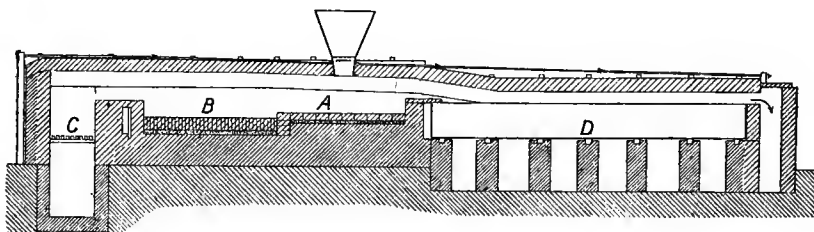


FIG. 15.—Old Type "Open" Black Ash Furnace.

oxide (Na_2O) formed (which reacts with the CaS present to regenerate Na_2S and Na_2S_2), but also the mass becomes hard and non-porous, and so difficult to lixiviate with water. The product at this stage is known as "black ash."

One of these furnaces takes a charge of some 150 kg. sodium sulphate (salt cake), and the operation is complete in about fifty minutes. The waste heat from the furnaces is usually utilised in evaporating the crude soda solution obtained by lixiviation (as described below), D being an iron tank containing the soda solution, over the surface of which the hot gases from the surface stream.

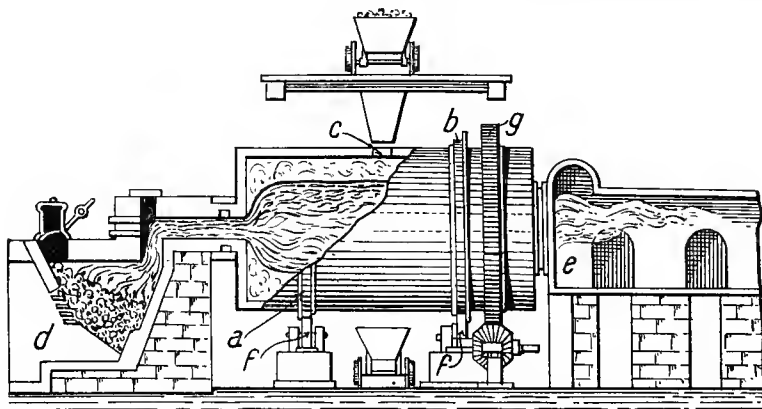


FIG. 16.—Revolving Black Ash Furnace.

The larger works, however, now usually employ large, mechanical, revolving black ash furnaces, shown in Fig. 16.

It consists of a large, horizontal, slowly revolving cylinder, some 10-15 ft. diameter, and 15-20 ft. long, made of boiler plate, and coated internally with fire-fast bricks or clay; an opening *c* serves either to fill or empty the cylinder. The hot gases and flames from the furnace *d* play through the interior of the cylinder as shown, and so uniformly heat the contents to a high temperature; the rotation of the cylinder (at first slow, but afterwards to 5-6 revs. per min.) thoroughly mixes the charge, and brings every portion under action of the flames. The hot furnace gases escape at *e*, and are utilised for evaporating the crude soda liquors from the lixiviating tanks as described in the open black ash furnace.

a and *b* are two steel bands on which the cylinder rotates, resting on the

friction wheels *f, f*. The whole is rotated by the massive cog-wheel *g*, the power being supplied by a steam engine.

The usual charge for a revolving black ash furnace of this type is 2 tons of sodium sulphate (salt cake), 2 tons of crushed limestone, and 1 ton of "slack" or powdered coal. The process is carefully watched by experienced workmen, and as the long yellowish green flames of carbon monoxide make their appearance, the operation is complete, and the cylinder is revolved until the opening *c* is just over an open iron truck. The door of the opening *c* is released, and the fused contents of the cylinder are discharged into the iron truck placed beneath. This truck runs on rails, and is drawn forward by means of an iron chain. As one truck fills, it is drawn forward and replaced by another. Finally the furnace is recharged, and the operation completed.

The whole process must be carefully controlled by experienced workmen, as too long or too short a period of heating will spoil the yield.

Process of Lixiviation.—The black ash so obtained consists of 39.45 per cent. Na_2CO_3 , 27.31 per cent. CaS , 9.11 per cent. CaO , and about 5.6 per cent.

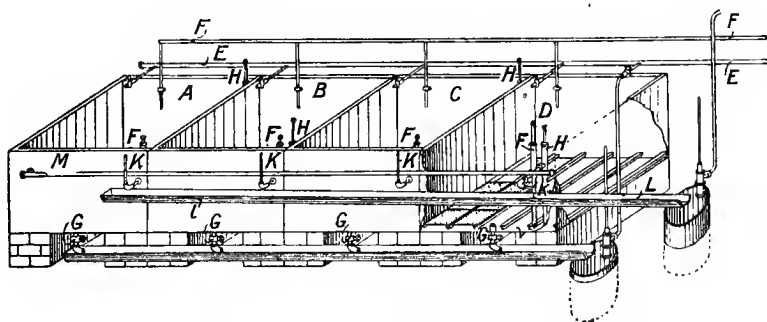


FIG. 17.—Shank's Black Ash Lixivating Tank.

of unaltered coal, together with small amounts of unaltered Na_2SO_4 , NaCl and silicates.

Fig. 17 shows Shank's process of lixiviation, the system which is now generally employed. A, B, C, D are a number of iron tanks (4-6), all of the same height, each provided with an inlet tube E for water, and with a steam pipe F for blowing steam into each tank with the object of maintaining the temperature of the contents of each tank at about 50°C ., thereby aiding the solution. G, G, G are outlet taps for running off the liquid contents of the several tanks. Each tank is also provided with two overflow pipes F and H, and with a false bottom of sieve-like or perforated nature.

The coarsely broken up black ash is placed on the perforated false bottom of all the tanks except one (which is put out of action for the purpose of emptying from extracted residues or for filling up with a fresh charge), and fresh water is allowed to flow from the water pipe E into the tank A, filled with black ash which already has been almost completely extracted. This incoming water floats upon the specifically heavier Na_2CO_3 solution in the bottom of the tank, and causes the liquid to flow through the overflow pipe H into the second tank B, where a still stronger solution of Na_2CO_3 is found. Here the same process continues, and so a stream of fluid of gradually increasing concentration flows in succession from one tank to another, until it reaches, say, the tank C filled with fresh black ash. Here the overflow pipe H is shut off, and so the saturated solution escapes by the overflow pipe F into the channel I, and is run off into the evaporating tanks. In the meantime, the tank D is recharged with fresh black ash, and the tank A is put out of action and emptied from the waste. So that B now forms the initial tank of the series and D the last, the saturated solution now issuing out of D. A is then refilled with fresh black ash, and becomes the last tank (B being put out of action and emptied), the connection between D and A being maintained by the pipe M.

This system has been in operation at St Helens since 1861. It is an application of the discontinuous counter-current principle.

There is left behind in the tanks, after the sodium carbonate and caustic soda have been crushed out, a mass of calcium sulphide (CaS), unchanged coal and

calcium carbonate. This is known as "**tank waste**" and is treated as described on p. 47.

The liquor drawn off is usually green in colour; it contains as impurities some thiosulphate and sodium sulphide in addition to excess of sodium carbonate and sodium hydrate. The specific gravity is usually 30° - 32° Bé. It should be noted that for rapid and complete extraction the black ash should be porous and contain some 10 per cent. or more of CaO , so that, when treated with water, the mass crumbles and swells up. The $\text{Ca}(\text{OH})_2$ formed converts part of the Na_2CO_3 into NaOH (see below).

The saturated black ash liquor can now be worked either for the manufacture of sodium carbonate or for the manufacture of caustic soda. We will take each in turn.

1. Working the Black Ash Liquors for Sodium Carbonate (Soda)

The liquid contains a considerable amount of caustic soda, " NaOH ," produced by the action of the free lime on the Na_2CO_3 . The first process, then, is to "carbonise" it by passing in CO_2 . The liquid is allowed to trickle down

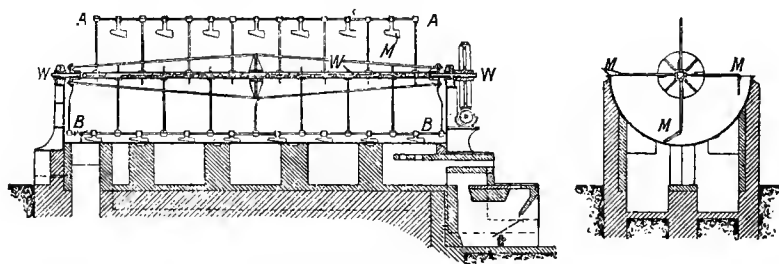


FIG. 18.—Thelen Evaporator.

tall iron towers, where it meets an ascending stream of CO_2 gas and air coming from limekilns. Sometimes the burnt gases from furnaces (also rich in CO_2) are used for this purpose. The CO_2 converts the NaOH into Na_2CO_3 ($2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$), and simultaneously Fe_2O_3 , Al_2O_3 , SiO_2 , etc., are precipitated, while oxygen in the hot entering gases oxidises the sulphides (e.g., Na_2S , FeS) to sulphates. The soda solution is now passed through filter presses and then is evaporated.

One process of evaporation much in vogue (on account of its cheapness) was the passage of the hot gases from the **black ash furnaces** over the **surface** of the liquor contained in tanks (see Fig. 15). The liquor thus becomes contaminated by ashes, etc., but by this "surface evaporation" the formation of hard firm crusts of soda at the bottom of the tank is avoided—an evil which at once results, if attempts are made to evaporate the liquors by heating from beneath, when these crusts settle and, like "boiler scale," greatly diminish the efficiency of the heating process.

This difficulty has been surmounted by the employment of special pans in which the bottom of the tanks are continually stirred by revolving arms, thus preventing the setting hard of solid crusts. Fig. 18 shows the well-known and very efficient **Thelen** evaporator.

It is set on brickwork and heated from beneath by the hot gases coming from the black ash furnace. The section is semicircular as indicated, and attached to a horizontal shaft, w w; running lengthwise down the pan are two other shafts A A, B B, to which are attached a number of wedge-

shaped scrapers *MMM*, loosely turning on the axle as these revolve about the central axle, and hanging vertically by their own weight when raised out of the pan.

As the main axle *W W* revolves the two subsidiary axes *A A*, *A A* revolve and the scrapers attached to them scrape the bottom of the pan as indicated in the cross section (Fig. 18).

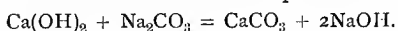
Any crystals of soda which separate out are scraped up by the scrapers out of the liquid and fall over the side of the pan, where the substance is shovelled away into vessels provided with a sieve-like bottom, from which the water drips away leaving the soda crystals to dry. When the evaporation takes place at a boiling heat the sodium carbonate crystals which separate out have the formula Na_2CO_3 . They are removed and heated more strongly (to completely dehydrate) in similar pans, but provided with crushing rollers, which run along the bottom of the pan, and are attached in a similar manner to rotating axes. The product is "soda ash," and is put on the market practically anhydrous, containing 98.99 per cent. of Na_2CO_3 ; 0.8 per cent. Na_2SO_4 ; 0.1 per cent. NaCl ; 0.1 per cent. sodium sulphite or sodium thiosulphate, with a little insoluble matter (less than 0.1 per cent. in good samples) and less than 0.7 per cent. of water.

In England this alkali is sold on the basis of the percentage of Na_2O it contains, an ash of the above composition being denoted as 58 per cent. alkali, *i.e.*, 100 parts contain 58 parts of Na_2O .

2. Working the Black Ash Liquors for Caustic Soda

The cheap and pure sodium carbonate obtained by the ammonia soda process (see below) has largely destroyed the market in England for Leblanc sodium carbonate, and consequently most English Leblanc alkali factories now work the black ash liquors directly for NaOH . There is a far more ready sale for caustic soda than sodium carbonate, because of the demand for the latter substance by industries such as the paper trade, the textile and cellulose (straw, etc.) industries, the oil and fat industry, soap makers, manufacturers of dyes (*e.g.*, Alizarin).

Owing to the presence of much free lime in the black ash the black ash liquors contain a very considerable amount of NaOH . The black ash liquor is diluted to 13° Bé. (= 13 per cent. NaOH in final liquor) and run into semispherical iron pans, in which are suspended wire cages filled with quicklime, CaO ; steam is driven through the liquid to maintain it at a boiling temperature, while a strong current of air pumped in at the bottom causes a thorough agitation of the contents and thus accelerates the causticisation which takes place according to the equation:—



The air blown in oxidises the sulphides of iron and sodium, the iron separating out at the bottom of the tank.

It should be noted that the solubility of lime, $\text{Ca}(\text{OH})_2$, in the liquor rapidly decreases with the amount of NaOH formed, and consequently a concentrated Na_2CO_3 liquor cannot be completely causticised by lime. Even a 10 per cent. Na_2CO_3 solution can only be causticised by lime to the extent of 97.3 per cent. However a very dilute solution would cause much expense and trouble in evaporating afterwards, and so in practice a moderately concentrated solution is taken, and the unchanged Na_2CO_3 is afterwards removed by crystallisation. The causticisation is greatly accelerated by heating, without, however, sensibly altering the equilibrium composition of the liquor. A much more complete causticisation is theoretically producible by using a more soluble base, such as strontium hydroxide, $\text{Sr}(\text{OH})_2$, or barium hydroxide, $\text{Ba}(\text{OH})_2$. Practically, however, the superior cheapness of lime more than compensates for the incomplete conversion of the sodium carbonate into caustic soda, and so lime is always employed for the purpose.

After the boiling has continued for a sufficient length of time, the liquid is allowed to settle, when the calcium carbonate (CaCO_3) and precipitated iron salts settle out at the bottom of the vessel, leaving a clear supernatant layer of NaOH . This is siphoned off clear, while the settled mud is washed on a filter. Finally the solution of NaOH is boiled down in multiple vacuum pans (such as is described in Martin's "Industrial Chemistry," Vol. I., under **Sugar**) made of cast iron. Almost invariably the process of evaporation is carried out in two distinct stages. First the liquor at 16°-17° Bé. is concentrated in one set of evaporators until a density of

26°-27° Bé. is attained. It is then run off into a second set of vacuum pans and boiled down until the density reaches 40° Bé., the Na_2CO_3 , NaCl , Na_2SO_4 , and other salts which crystallise out as the concentration proceeds being separated by passing the liquor through filters interposed between the various vacuum pans. Finally the concentrated liquor is run out into thick cast-iron semispherical pots, set in brickwork over a free fire, and capable of holding some 10-15 tons of NaOH . Here the boiling down is continued, the pots being finally heated to 400°-500° C., the NaOH being actually fused.

Now the caustic soda obtained by the Leblanc process always contains much impurity, principally sodium sulphide (Na_2S), iron sulphide (FeS), and also sodium cyanide (NaCN), in the form of ferrocyanide derived from the nitrogenous matter in the coal used for melting the sodium sulphate. The product is therefore purified by adding sodium or potassium nitrate to the molten mass, whereby the sulphides are completely oxidised and the ferrocyanides are destroyed with separation of graphite, while the iron separates as a red precipitate of ferric oxide. As Ralston showed in 1860, when the caustic soda is anhydrous all the iron separates, and the addition of only a handful of nitre will cause a large pot containing some 16 tons of molten NaOH to change from yellow, through white, to green or vice versa. Too much nitre must not be added as it colours the molten mass greenish owing to the formation of a trace of manganate.

After partial cooling, during which the very considerable precipitate of iron hydroxide, etc., is allowed to settle out at the bottom, the still molten caustic, which is as clear and limpid as water, is ladled out into thin sheet-iron drums, allowed to solidify, and the drums soldered up air-tight as soon as the caustic soda has set. Occasionally the solid mass is smashed into lumps before packing in iron drums (which are soldered up air-tight). Sometimes the NaOH is ground to a powder in special machines provided with precautions against the escape of NaOH dust into the air, and the powdered NaOH is then packed as before.

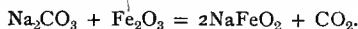
"White caustic," as colourless caustic soda is called, was first manufactured by this process from Leblanc soda about 1862, and is now put on the market containing as much as 76 per cent. of alkali, other strengths being made, however, down to 60 per cent. alkali.

Caustic soda is manufactured in exactly the same way from the sodium carbonate prepared from the ammonia soda process. The initial raw material is here "calcined soda," and the only difference in the mode of preparation is that the NaOH thus produced is somewhat purer, so that the addition of nitre in the final fusion of the NaOH is unnecessary. The principal impurities in the NaOH made from ammonia soda sodium carbonate is NaCl and unchanged Na_2CO_3 .

These impurities, however, do not cause any trouble in the application of the NaOH for many industrial purposes, e.g., soap making, as the soap itself often contains 20 per cent. and more NaCl .

Among other processes for making caustic soda we must here mention the **Löwig process** employed by the Solvay Works.

Calcined sodium carbonate (soda ash), or sodium bicarbonate prepared by the ammonia soda process, is employed. The substance is mixed with iron oxide and heated in a revolving cylinder furnace similar to the revolving cylinder black ash furnace described above. The last furnace gases and flames streaming through the interior of the cylinder heat the mass to redness when the following action takes place:—



All the CO_2 escapes, and the resulting sodium ferrite (NaFeO_2) is raked out and lixiviated with water, when it decomposes according to the equation:—



A concentrated solution of NaOH is immediately obtained, under which the iron oxide settles out as a dark mass. The NaOH solution, in a practically pure condition, is drawn off, evaporated, and melted as above described, no nitre being necessary for the final melting.

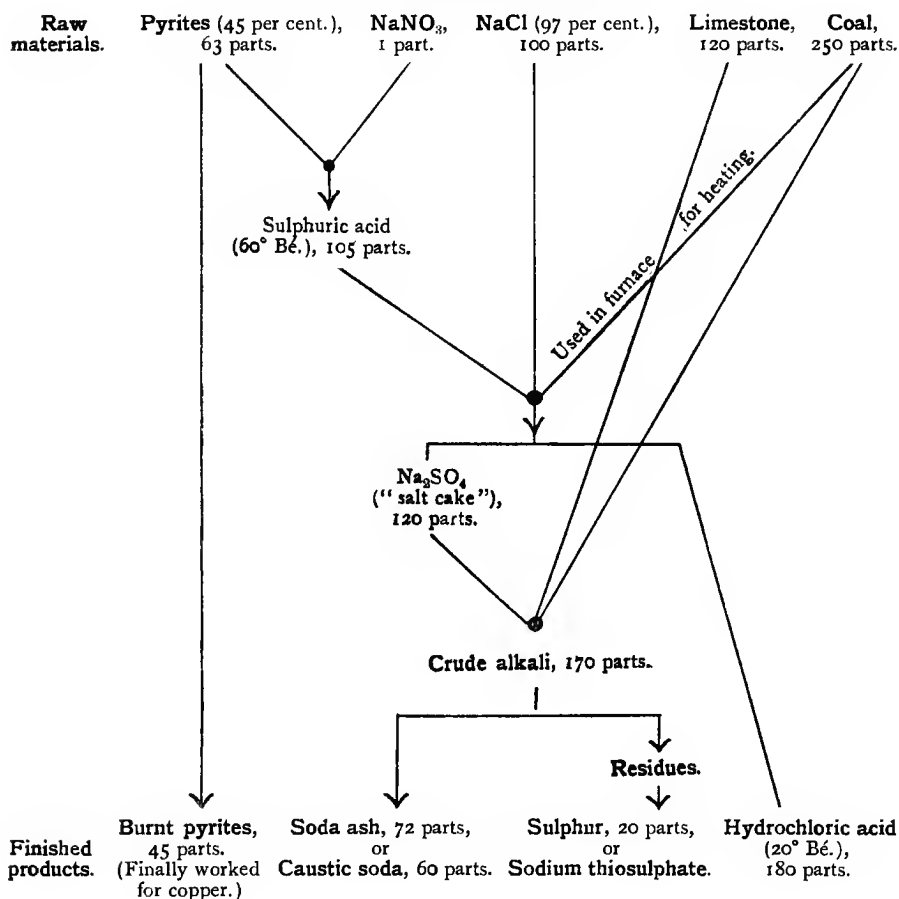
Considerable amounts of caustic soda and caustic potash are prepared by the **electrolysis of NaCl or KCl solutions**. These processes are described in detail under the heading "Chlorine Industry" (Martin's "Industrial Chemistry," Vol. II.), and so we will not further deal with them here, except to say that the NaOH or KOH solutions drawn off are evaporated as above described in vacuum

pans, freed from NaCl or KCl, crystallising out, and finally melted in large iron pots (see p. 46).

The mercury diaphragm process yields a chlorine-free NaOH or KOH, while that obtained by the diaphragm process yields an NaOH (or KOH) solution rich in NaCl (or KCl). However, the NaCl (or KCl) almost entirely crystallises out during the concentration of the solution, being very insoluble in concentrated NaOH solution. Where the NaOH solution is not immediately used for Alizarin manufacture (see Martin's "Industrial Chemistry," Vol. I., Organic), it is boiled down, fused, and packed in iron drums for transport or export as above described.

SUMMARY OF THE LEBLANC PROCESS.

(After Ost, slightly modified.)



In England the **strength of the caustic soda** is expressed on the basis of the percentage of Na₂O it contains. Thus a pure NaOH (100 per cent. NaOH) would be in England denoted as 77.5 per cent. caustic soda, since 100 parts of NaOH contain 77.5 parts of Na₂O.

In Germany, however, its strength is calculated on the supposition that this Na₂O is combined as Na₂CO₃, *e.g.*, a 100 per cent. NaOH in Germany would be denoted as a 132.5 per cent. caustic soda (because 100 parts of NaOH are equivalent to 132.5 parts of Na₂CO₃).

For details the reader should consult Keane-Lunge, "Technical Methods of Analysis."

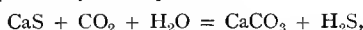
Treatment of Alkali Waste.—After the lixiviation of the black ash for sodium carbonate and caustic soda (see p. 44), there is left behind in the tanks a mass of calcium sulphide, together with unchanged coal and unchanged calcium

carbonate, lime, etc. ($\text{Na}_2\text{SO}_4 + \text{CaCO}_3 + 2\text{C} = \text{Na}_2\text{CO}_3 + \text{CaS} + 2\text{CO}_2$), the product being known as "tank waste" or "alkali waste."

To every ton of soda produced nearly a ton of these residues accumulated, which formerly were an intolerable nuisance, since by the action of atmospheric acids on the calcium sulphide, sulphuretted hydrogen (H_2S) was set free, poisoning the air in the neighbourhood. Also the drainage from the mass, containing as it did soluble sulphur-containing compounds and sulphuretted hydrogen, was very harmful. This mass also contained the total sulphur introduced into the process (as Na_2SO_4), which was therefore lost.

This waste mass is now worked for **sulphur** by the **Chance-Claus process**, the sulphuretted hydrogen being either burned in a Claus kiln to produce sulphur, as described in Martin's "Industrial Chemistry," Vol. II., or else it is burned to SO_2 and converted into sulphuric acid.

The Chance process is expressed by final equations :—



from which it is obvious that the calcium carbonate (CaCO_3), originally introduced into the process, is again capable of being recovered and used again. Since the sulphur is also recovered in the form of H_2S (and ultimately as S or H_2SO_4) there is now no more "waste" theoretically produced by the Leblanc process. Sometimes the waste residues are worked for sodium thiosulphate (hyposulphite) ($\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$), as described in Martin's "Industrial Chemistry," Vol. II.

It is said that 30,000-40,000 tons of sulphur are annually recovered by this process in Great Britain.

It can be safely stated that without the Chance-Claus process, Leblanc soda would long have become entirely defunct, not only on account of the financial loss of the sulphur, but also on account of the objectionable nature of the alkali waste itself, which weathers and oxidises, producing H_2S and SO_2 , even catching fire occasionally, and the drainage from which is naturally an exceedingly unpleasant and harmful liquor.

CHAPTER VI

Manufacture of Sodium Carbonate by the Ammonia Soda Process

CHAPTER VI

MANUFACTURE OF SODIUM CARBONATE BY THE AMMONIA SODA PROCESS

LITERATURE

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Present Position of the Ammonia Soda Process.—The manufacture of sodium carbonate by the ammonia soda or Solvay process occupies to-day a predominant position in the chemical industry. During the period, 1864-1868, the annual output of soda ash by this process amounted to 300 tons. In the year 1902 it had grown to 1,600,000 tons, whilst at the present time the total production probably exceeds 3,000,000 tons per annum.

During the years 1879-1883 the output by the Leblanc process reached a maximum of 500,000 tons per annum. Since that time the Leblanc industry has steadily declined, and were it not for the recovery of by-products and the large amount of capital invested in this process, it is probable that the production of the Leblanc alkali would by this time have entirely ceased.

The manufacture of bleaching powder with the aid of electrolytic chlorine has considerably affected the Leblanc industry, and doubtless this influence will be felt even more seriously in the future.

The ammonia soda process produces sodium carbonate in a higher state of purity and at a much lower cost than the Leblanc process. Recently competition and a desire to stimulate the demand for ammonia alkali has resulted in a considerable reduction in the price of this article, with the consequence that it is almost impossible for the makers of soda ash by the Leblanc process to compete.

The ammonia soda process itself will soon be confronted with competition by the exploitation of natural deposits of soda which occur near Lake Magadi, in East Africa. A company has been formed with a capital of £1,300,000 to mine

these deposits, which have approximately the following components:— Na_2CO_3 , 43.5; NaHCO_3 , 40.4; H_2O , 15.6; NaCl , 0.4.

Factories are being erected in England and in the East to refine the raw material and to convert it into other soda compounds (see p. 35). It has, however, to be remembered that the cost of an article to the consumer is largely determined by the expense of carriage, and this item, with regard especially to the natural soda, must necessarily be in most cases particularly heavy.

Another disturbing factor in the ammonia soda industry is the ever-increasing production of caustic alkali by electrolytic processes. In a very large number of industries the soda ash is only used after causticising by lime, with the consequence that, should it be possible to produce caustic soda at a sufficiently low price, very serious competition with ammonia soda would result.

As, however, it will be pointed out later, the ammonia soda process has been brought to an exceedingly high state of economic efficiency, and in spite of the various factors mentioned, it is questionable whether the commanding position which it at present holds in the alkali industry is seriously threatened.

Historical.—It is not proposed to deal in this article at any length with the historical aspect of the ammonia soda process. The reader who is interested in the subject may be referred to *Mond, Journ. Soc. Chem. Ind.*, 1885, p. 527. Also to a lecture given by Ernest Solvay at the **International Congress of Applied Chemistry**, Berlin, 1903. A copy of this will also be found in *La Revue de l'Université de Bruxelles*, May 1903.

In 1838 the treatment of brine with carbonate of ammonia was patented by Dyar and Hemming, and subsequently by Delaunay in 1839. In 1840 the introduction of carbon dioxide in the gaseous form was also patented by Canning. Subsequently in 1852, Crinus, a Frenchman, directs the recovery of the gas given off in the calcination of the sodium bicarbonate, whilst Chisholm in the same year patents the distillation of ammonium chloride with lime, and the subsequent absorption of the gas in brine. The application of this had been anticipated, however, by Delaunay.

Thus already, in 1852, all the chemical reactions essential to the success of the ammonia soda process were well known, and it is significant that from that time onwards all the patents taken out which had any subsequent bearing on the history of the industry related to the disposition and nature of the apparatus to be employed, and it is in this connection that the ammonia soda process is indissolubly connected with the name of Solvay. From 1861 onwards, Ernest Solvay, with the assistance of his brother Alfred, devoted his attention to the perfection of the mechanical details of the plant, and in 1863 *La Société Solvay et Cie* was formed with a capital of 136,000 francs for the erection at Couillet of a factory to produce sodium carbonate by this process. In the year 1866 the production of this factory reached one and a half tons per day.

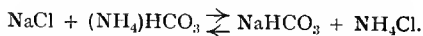
In 1872 Ernest Solvay was approached by Ludwig Mond, with the consequence that the process was also started at Northwich, in Cheshire. The factory now at Winnington, near Northwich, owned by Brunner, Mond & Co., is probably the largest in the world, producing, as it does, about 200,000 tons per annum. This company now also owns works at Lostock Gralam, Middlewich, and Sandbach, all in the Cheshire brine district, so that the total output of this firm will be in the neighbourhood of 500,000 tons per annum.

The firm of Messrs Brunner, Mond & Co. forms part of the powerful Solvay syndicate which practically controls the ammonia soda industry of the world, owning, as it does, works all over the Continent of Europe and in the United States of America. Besides the works owned by Messrs Brunner, Mond & Co., only two other ammonia soda factories exist in England, that of the United Alkali Co., at Fleetwood, in Lancashire, and that of the Ammonia Soda Co., at Lostock Gralam, in Cheshire.

In America several factories outside the combine exist, notably the Michigan Alkali Co., the Columbia Chemical Co., and the Mathieson Alkali Co.

On the Continent a new factory outside the combine, the *Adriawerke Aktiengesellschaft*, Trieste, has recently commenced operations.

Theoretical Considerations.—The fundamental reaction on which the ammonia soda process depends is of the simplest character, and may be expressed by the equation—



A consideration of the solubility of these salts in water will indicate in which direction we may expect the reaction to proceed, and in consequence which salts, if any, we may expect to be precipitated.

The following table shows the solubility of NaCl , NaHCO_3 , and NH_4Cl in water:—

SOLUBILITY OF NaCl IN WATER.

Temperature. Degrees.	Grams in 100 g.
10	35.69
20	35.82
30	36.03
40	36.32
50	36.67
60	37.06

NaHCO ₃ in H ₂ O.		NH ₄ Cl in H ₂ O.	
Temperature. Degrees.	Grams in 100 g.	Temperature. Degrees.	Grams in 100 g.
0	6.9	0	29.7
10	8.2	10	33.3
20	9.6	20	37.2
30	11.1	30	41.4
40	12.7	40	45.8
50	14.5	50	50.4
60	16.4	60	55.2

Sodium bicarbonate (NaHCO₃) is by far the least soluble of all these salts, and it would thus be anticipated that the first salt to be precipitated would be sodium bicarbonate. The probability that such will be the case becomes still greater when one investigates the solubility of sodium bicarbonate in solutions of sodium chloride, ammonium bicarbonate, and ammonium chloride.

SOLUBILITY OF NaHCO₃ IN NaCl (Fedotieff, *loc. cit.*).

NaCl.	NaHCO ₃ .
Grams per Litre.	Grams per Litre
0	105.8
172	29.0
231	20.1
313	12.1
0	85.3
175	21.4
234	14.6
312	8.8

} at 30° C.

} at 15° C.

SOLUBILITY OF NaHCO₃ IN NH₄HCO₃.

NH ₄ HCO ₃ .	NaHCO ₃ .
Grams per Litre.	Grams per Litre.
0	85.3
21.1	77.0
79.8	62.1

} at 15° C.

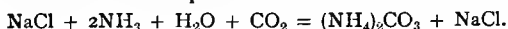
SOLUBILITY OF NaHCO₃ IN SOLUTIONS OF NH₄Cl AND NaCl (Schreib).

100 c.c. of a solution containing 18 g. of NH₄Cl dissolved before and after the addition of NaCl, gives the following quantities of NaHCO₃ :—

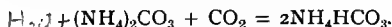
At 25° C.			At 40° C.		
NH ₄ Cl.	NaCl.	Na ₂ CO ₃ as NaHCO ₃ .	NH ₄ Cl.	NaCl.	Na ₂ CO ₃ as NaHCO ₃ .
0	0	6.5	0	0	8.0
18	0	6.0	18	0	7.0
18	2	5.0	18	2	6.2
18	8	2.7	18	8	3.8
18	14	1.7	18	14	2.3

Thus in each case the solubility in the saline solution is much lower than in water.

If, then, a current of carbon dioxide be passed through brine containing ammonia gas in solution, the following reaction will first of all take place:—



The effect will be the formation *in situ* of a solution of the normal carbonate of ammonia, when all the ammonia present has been converted into the normal carbonate. Further passage of carbon dioxide will result in the formation of the acid carbonate—



We shall in consequence have a system containing the ions—



The value of the solubility product $[\text{Na}^+][\text{HCO}_3^-]$ in the solution of sodium chloride is, of course, lower than in water, owing to the depression of the dissociation of the feebly ionised sodium carbonate by the strongly dissociated sodium chloride containing the common ion Na^+ , and when a certain quantity of carbon dioxide has passed, the solubility product $[\text{Na}^+][\text{HCO}_3^-]$ is exceeded, and precipitation of sodium bicarbonate results. Were the passage of carbon dioxide now stopped no further precipitation would occur. As, however, more carbon dioxide is bubbled through the solution, it is absorbed by the ammonium carbonate, giving ammonium bicarbonate. In this way the concentration of the HCO_3^- ion is renewed, and as there is a large excess of Na^+ ions present, the value of the solubility product is again exceeded, and so precipitation proceeds. Gradual depletion of the Na^+ ions from the solution, together with the fact that no more carbonate of ammonia is present, by means of which the concentration of the HCO_3^- ions may be increased, results eventually in a point being reached when the value of the solubility product $[\text{Na}^+][\text{HCO}_3^-]$ does not exceed the limiting value but is equal to it, with the consequence that equilibrium is established. Owing to the smaller value of the solubility product at a lower temperature, a reduction in the temperature of the solution at this point would, of course, lead to further precipitation. Thus for any given temperature the equilibrium will be represented by the expression:—

$$\frac{[\text{NaHCO}_3][\text{NH}_4\text{Cl}]}{[\text{NaCl}][\text{NH}_4\text{HCO}_3]} = K.$$

These considerations indicate the conditions necessary to obtain the maximum yield of sodium bicarbonate. It is apparent that—

1. *The solution must originally contain a very high concentration of the Na^+ ions, i.e., it must be fully saturated with salt.*
2. *The solution must contain a high concentration of ammonia in order that by subsequent absorption of carbon dioxide the greatest number of HCO_3^- ions may be produced.*
3. *To decrease the value of the solubility product $[\text{Na}^+][\text{HCO}_3^-]$, the temperature of the solution must be low.*

Unfortunately, for many reasons, both chemical and industrial, it is impossible to realise the ideal conditions.

When a solution of sodium chloride is treated with ammonia gas, the concentration of the sodium chloride falls as the concentration of the ammonia increases. This is shown by the following table:—

SOLUBILITY OF SODIUM CHLORIDE IN SOLUTIONS OF AMMONIA AT 30° C.

(Hemple and Tedesco, *Zeit. angew. Chem.*, 1912, 24, 2468.)

NaCl.		NH_3 .		Specific Gravity.
Grams per Litre.	Grams, Molecules per Litre.	Grams per Litre.	Grams, Molecules per Litre.	
293.38	5.4836	29.535	1.7374	1.1735
292.50	4.9972	40.635	2.3915	1.1656
289.70	4.9500	47.260	2.7800	1.1600
286.50	4.8950	60.780	3.5750	1.1494
283.38	4.8426	72.070	4.2390	1.1406
283.06	4.7942	72.715	4.2772	1.1395
277.49	4.7413	81.855	4.8150	1.1301
270.57	4.6123	97.490	5.7348	1.1205

Further, in practice the ammoniacal solution of salt is always to some extent diluted by water vapour carried over with the ammonia gas, and it is found impossible during the precipitation of the sodium bicarbonate to work at very low temperatures. This matter will again be referred to later.

It is thus necessary to consider what is the most suitable concentration in ammonia to which the brine should be brought, in order that the maximum yield of sodium bicarbonate may be obtained under industrial conditions. In the domain of pure chemistry the problem has been attacked from the standpoint of the phase rule by various workers.

Schreib ("Ammonia Soda," *loc. cit.*) gives the results obtained on carbonating, under the same conditions, solutions containing varying concentrations of salt and ammonia. The experiments were carried out with only approximate accuracy, but nevertheless are comparative amongst themselves.

Some of Schreib's figures are here given :—

	Original Solution.		Carbonated Solution.			Per Cent. of NaCl Converted.	Na ₂ CO ₃ as NaHCO ₃ . Grams per Litre.
	NH ₃ per Cent.	NaCl per Cent.	NH ₃ per Cent.	NaCl per Cent.	NH ₄ Cl per Cent.		
1	6.3	27.4	1.2	10.9	16.4	62.5	138
2	6.6	27.3	1.3	10.2	16.1	63.1	146
3	7.2	27.2	1.3	9.3	17.9	67.8	154
4	8.9	25.8	...	7.4	18.8	73.6	168
5	11.5	24.3	1.3	7.3	18.5	73.6	145

The solutions used in practice will correspond to Nos. 3 and 4, although so high a conversion as 73.6 per cent. of the NaCl into NaHCO₃ will not usually be attained, as the carbonating operation for various reasons is never carried on to its extreme limit.

Fedotieff (*loc. cit.*) determined the solubility of the four salts in the presence of one other. He then took weighed quantities of the NaCl, NH₄HCO₃ and H₂O, and shook them in a closed vessel for several hours at 15° C. In this way the following results were obtained :—

In 1,000 g. of Water.			Solutions Containing Gram Equivalents per Litre.				Per Cent. Decomposition of NaCl.
NaCl.	NH ₄ HCO ₃ .	NH ₃ .	HCO ₃ '.	Cl'.	Na'.	NH ₄ '.	
336	336	72.4	0.3	4.74	1.78	3.46	62.5
336	377	81.3	0.64	4.65	1.47	3.82	68.5
340	416	89.6	0.77	4.67	1.25	4.19	73.4

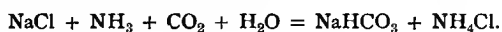
By means of a space model and graphical extrapolation he deduced that a maximum decomposition of 83.4 per cent. of NaCl could be obtained in this way at a temperature of 30° C., and indicated that at 15°-20° C. in industrial practice a conversion of 79-80 per cent. NaCl should be possible. He further points out that theoretically it is better to treat common salt, either solid or in solution, with solid ammonium bicarbonate as in the process of Schlösing (English Patent, 21,370, 1878; 2,110, 1882; 4,025, 1885).

Janecke (*loc. cit.*) applies his graphical method of representing reciprocal pairs of salts (*Zeits. anorg. Chem.*, 1906, 51, 132-157) to the problem, and demonstrates the possibility of increasing the yield by the addition of solid NaCl whilst the solution is maintained at 32° C.

As has previously been mentioned, the concentration of salt and ammonia in the ammoniacal brine cannot be determined by purely theoretical conditions. It has already been pointed out that the concentration of the salt in the ammoniacal brine is diminished to some extent by water vapour carried over from the ammonia stiller. Again, it is found in practice more difficult to prepare solutions containing a high concentration of ammonia than those containing a low concentration.

When working with solutions containing a high concentration of ammonia the yield of sodium bicarbonate is better, and the more concentrated liquor returning to the ammonia stills requires less steam for distillation and less effluent is produced. The carbonating process is, however, much slower and there is more danger during the treatment of these strong liquors of losing ammonia.

The ammonia soda process in outline (see also p. 73) may be summarised as follows: Brine (NaCl) is saturated with ammonia gas (NH₃), and subjected to the action of a current of carbon dioxide (CO₂), produced by the burning of limestone, when the following reaction takes place :—



The bicarbonate of soda (NaHCO_3) so produced is filtered and calcined ($2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{CO}_2$); the evolved CO_2 , being used against the mother liquor containing NH_4Cl , is returned to the ammonia distiller, where, by treatment with lime and steam ($2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 = \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$), the ammonia is recovered and again absorbed in fresh brine. The spent liquors (containing CaCl_2 and NaCl), after extraction of the ammonia, pass away as the effluent.

Operations on the Industrial Scale

Preparation of the Saturated Solution of Salt.—It is essential to the commercial success of the ammonia soda process that an abundant supply of sodium chloride, either as rock salt or as fully saturated brine, preferably the latter, be close at hand. Some factories are at work where the salt has to be transported to the works, but it is probable that, unless the price of soda ash in the country under consideration were not artificially maintained, they would have great difficulty in competing.

Where rock salt mines exist, as at Fleetwood in Lancashire, it is usual to flood these with water and to subsequently pump away the brine formed by the dissolution of the rock salt (see p. 5, **Salt Industry**).

The utilisation of the salt in the process is by no means complete, only 60 per cent. to 73 per cent. of the sodium chloride being converted into sodium bicarbonate, and for the production of 1 ton of soda ash it will be necessary to treat 7·8 tons of brine.

Natural brine contains impurities such as calcium and magnesium salts (see p. 7).

A typical analysis of natural brine (Cheshire) is given below :—

	Grams per Litre.
NaCl	300.0
MgCl_2	0.6
MgSO_4	0.7
CaSO_4	4.0
CaCO_3	0.2

Formerly these impurities were removed before the brine entered the process, by treatment of the crude brine with sodium carbonate and lime. This, however, is not the usual practice at the present day, and the impurities which are precipitated during the saturation of the brine with ammonia containing carbon dioxide are removed at a later stage.

The brine, from whatever source it may be obtained, is usually pumped into large reservoirs. From these reservoirs it is again pumped to a tank at the top of the main building, so that it may gravitate from there to the washers and absorber, and subsequently to the settling vats.

Saturation of the Brine with Ammonia.—Several different forms of ammonia absorber have been used from time to time. They all depend for their construction on the simple principle of allowing the gas from the ammonia distiller to meet a stream of brine after the manner of counter-currents.

A typical absorber is shown in Fig. 19. The brine flows downwards, through the various compartments, whilst the ammonia gas by means of the serrated mushrooms is caused to bubble through the liquor in each compartment. This type of apparatus is very widely used in the industry for numerous operations.

The "tower" washer, Fig. 20, is of similar construction, but larger. It is used for recovering the ammonia carried away by the gas current from the carbonating plant. A portion of the brine which enters the absorber will first pass through this column.

The gases entering the ammonia absorber consist of ammonia, carbon dioxide (resulting from the decomposition of the sodium and ammonium bicarbonates present in the mother liquor), and water vapour, together with small quantities of air which

have been previously present in the liquors, or in the water from which the steam necessary for distillation was generated. In addition a certain amount of sulphuretted hydrogen will be present, due to the use of crude gas liquor, to make up for any losses in ammonia that occur.

The ammonium sulphide thus formed reacts with the iron of the vessel to produce a thin coating of sulphide of iron; this prevents the dissolution of the metal by the liquors which otherwise would result in a discoloration of the finished product.

During the distillation of **1 metric ton** of ammonia there will enter the absorber at a temperature of $60^{\circ}\text{C}.$, in addition to the 1 ton of ammonia, 720 kilos of CO_2 , 380 kilos of H_2O .

The absorption of the ammonia by brine, of the carbon dioxide by the ammoniacal brine, and the condensation of the water vapour, results in the evolution of large quantities of heat, with the consequence that the total amount of heat evolved will be approximately 900,000 kilo calories per metric ton of ammonia distilled. This will be sufficient to raise the 12,500 kg. of liquor in which the ammonia will dissolve by about $72^{\circ}\text{C}.$

It is essential that the temperature of the liquor in the absorber should be maintained as low as

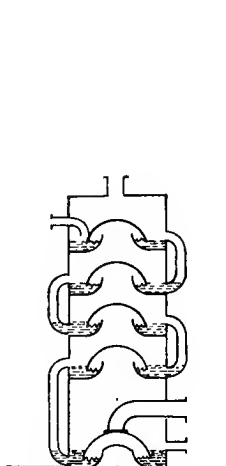


FIG. 19.—Ammonia Absorber.

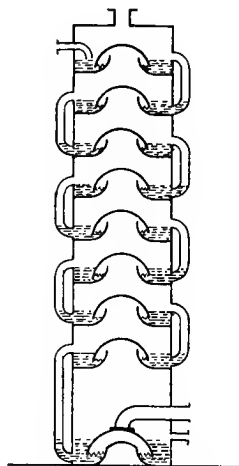


FIG. 20.—Ammonia Recovery Tower.

possible, in order to keep down the partial pressure of the ammonia in the liquor, and thus assist absorption. This is especially necessary when, as is now the case, the absorber is worked under a vacuum. Further, at a high temperature the ammonium carbonate is decomposed, and a loss of carbon dioxide will result.

Unfortunately any cooling pipes inserted inside the vessel so soon become coated over with a heat insulating scale of calcium and magnesium carbonates as to render them almost inoperative. They must in consequence either be very frequently cleaned, or some other method must be adopted of keeping the temperatures down. It will suffice here to say that the temperature is so regulated as not to exceed $60^{\circ}\text{C}.$

The gas leaving the absorber will still contain a fair quantity of ammonia. It is in consequence passed through another tower, where it can again be submitted to the action of fresh brine. Finally it may, if necessary, be passed through another washer containing water in order that the last traces of ammonia may be removed. This final washer is in direct connection with an air pump, which maintains a vacuum through the washers and absorber to the ammonia still.

Part of the fresh brine entering the process passes first of all through the carbonating or tower washer, where any ammonia mechanically carried over by the gas current from the precipitating apparatus is recovered. It then joins the brine, leaving the absorber washer before entering the absorber itself.

It may here be pointed out that ammonia gas is absorbed by brine with great avidity. Thus in an experimental plant the author found that by bubbling 2,000 kilos per hour of NH_3 gas over a surface of 3 sq. m. through 6 in. of brine already containing 40 g. per litre of NH_3 , 1,000 kilos per hour were absorbed when the temperature was maintained even as high as 70°C ., and the resulting liquor contained 80 g. per litre of NH_3 .

The liquor leaving the absorber will have approximately the following composition:— NaCl , 260 g. per litre; NH_3 , 80 g. per litre; CO_2 , 45 g. per litre. It will contain in suspension as carbonates all the calcium and most of the magnesium salts originally present in the brine. In order to clarify this liquor, it flows by gravity to the bottom of a large tank, and is allowed to overflow from the top of this vessel to the bottom of another, and so on, until eventually the liquor arrives at the final tank perfectly free from all suspended matter.

Several hundred tons of liquor may thus be kept continuously settling. In this way not only is the clarification of the liquor accomplished, but the liquor leaving the last vessel is maintained at a constant strength, and the effect due to any irregularities in the working of the absorber is

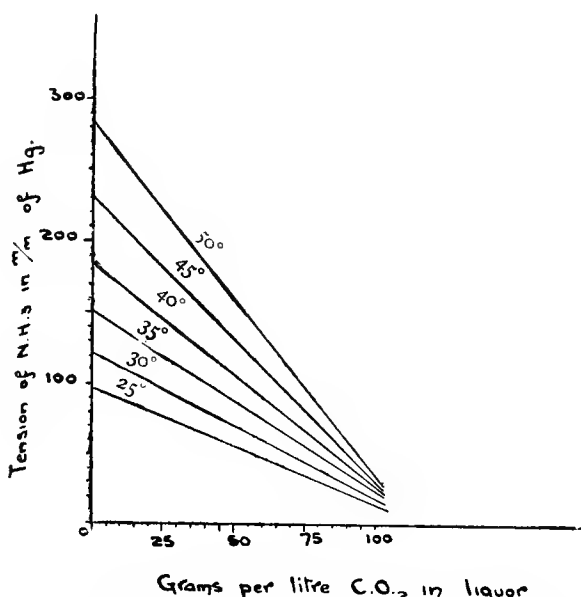


FIG. 21.—Influence of Temperature and CO_2 content on tension of NH_3 in Solutions of Ammoniacal Brine.

minimised. The mud separating out in the settling vats may be kept in a state of suspension by an agitator, and passed to another vessel, where it is washed with brine or water; alternately it may be pumped direct to the ammonia stills in order that the ammonia present may be recovered.

Carbonating Apparatus.—The clear ammoniacal brine leaving the last settling or storage tank must be cooled down before it is subjected to the action of the carbon dioxide. Otherwise a large quantity of ammonia will be carried away by the gas current to the carbonator washer.

It is interesting here to note that the amount of ammonia thus removed from solution is dependent not only on the temperature, but also on the content of carbon dioxide in the liquor, for as the concentration of carbon dioxide in the liquor increases, so the tension of the ammonia in solution decreases, with the consequence that the higher is the concentration of carbon dioxide in the ammoniacal brine entering the carbonating apparatus, the smaller will be the quantity of ammonia carried away by the gas current. The influence of temperature and of the carbon dioxide content in the tension of ammonia in solutions of ammoniacal brine as determined by the author is shown in Fig. 21.

The curves refer to a solution containing 80 g. per litre of ammonia, and 270 g. per litre of sodium chloride.

In order to cool the ammoniacal brine it is pumped through a cooler of the evaporative type, whereby the liquor passes through a number of cast-iron pipes over which cold water is running.

Owing to the fact that the insoluble magnesium salts do not readily separate from solutions of ammoniacal brine, a portion of the magnesium salts present is precipitated on the interior of these cooling pipes as an intensely hard scale. The composition of this scale varies somewhat. It was found by Reinitzer, *Zeits. angew. Chem.*, 1893, 446, to consist of $\text{MgCO}_3 \cdot \text{NaCl}$.

The effect of this scale formation is to rapidly diminish the cooling effect of the apparatus, and in consequence the pipes must periodically be steamed out, and the scale removed.

The ammoniacal brine, cooled to about 30°C. , is now ready to enter the carbonating apparatus. Various forms of carbonators have been devised, but it will be sufficient here to describe the apparatus used by Solvay and that introduced by Honigmann, D.R.P., 13,782.

Amongst other types of carbonating plant that have been used may be mentioned that introduced by Boulouvard, French Patent, 125,625, 1878, and by Schreib, D.R.P., 70,169.

In the Solvay apparatus (Fig. 22) the liquor is pumped to the top of a high tower, where it falls over a series of baffle plates and meets, after the manner of counter-currents, a stream of carbon dioxide gas rising upwards. The absorption of the carbon dioxide by the ammoniacal brine results in the evolution of considerable quantities of heat, and in order to keep down the temperature of the liquor the lower portion of the tower is fitted with the well-known Cogswes coolers (English Patent, 1,973, 1887), which consist of a number of mild steel tubes expanded into a steel tube plate. The liquor as it reaches the bottom of the tower falls over these tubes through which cold water is running. The Solvay tower may be from 70-90 ft. high, and from 5-7 ft. in diameter.

It is the usual practice now to conduct the carbonating operation in two stages. In the first tower the absorption of the carbon dioxide is allowed to proceed up to the point when most of the ammonia present, but not all, has been converted into the normal carbonate. From the bottom of this tower the liquor may be blown into a storage tank, and thence pumped to the top of the second tower, known as the precipitating or making tower. Here further absorption of carbon dioxide goes on, and the sodium bicarbonate is precipitated. It is necessary to regulate with great care the temperature of the liquor during this operation. If the temperature is kept too high the sodium bicarbonate is of very coarse grain, and although well suited for the **Thelen pans**, it may not filter so well nor be so easily washed as material of a finer grain. At the same time the yield is, of course, considerably decreased, not only owing to the greater solubility of the salt at the higher temperature, but also owing to the increased partial pressure of the carbon dioxide in solution, and the consequent decreased efficiency with which the carbon dioxide is absorbed. It must be remembered that only so long as the partial pressure of the carbon dioxide in the gas exceeds the partial pressure of the carbon dioxide in the liquor can absorption proceed.

Should the temperature of the liquor be brought too low, the resulting sodium bicarbonate is of a pasty consistency. It is almost impossible to filter or wash the material, and on calcining in the **Thelen pans** it is discharged in the form of small balls, the outside of which is the normal carbonate, whilst the interior is a core of the bicarbonate of sodium.

The magma of bicarbonate of soda and ammoniacal liquor is blown by the gas pressure from the precipitating tower to the filtering plant. The temperature of the liquor leaving the carbonating tower will be about 30°C. or less. It may, however, be mentioned here that it is not so much the final temperature of the liquor which affects the grain of the bicarbonate of soda, as the conditions existing in the tower before that temperature is reached.

Obstructions in the form of hard crusts of sodium bicarbonate gradually form in the precipitating tower, with the consequence that at intervals the towers must

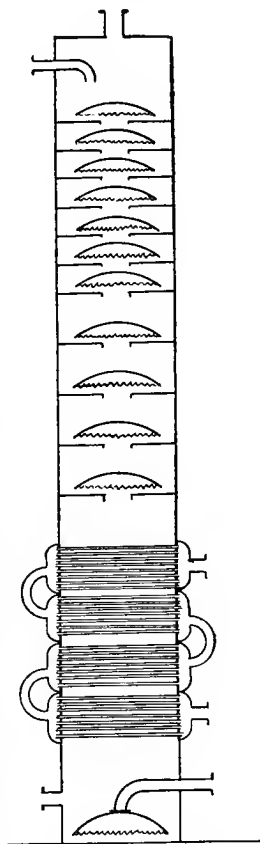


FIG. 22.—Solvay Tower.

either be changed over so that the fresh ammoniacal brine is pumped through the precipitating tower in order to dissolve these crusts, or the tower may be treated with steam and the dissolution of the crusts effected in this way.

The liquor leaving the first Solvay tower may contain up to 90 g. per litre of carbon dioxide, whilst the liquor entering the filter will have been carbonated to such an extent that it contains about 20 g. per litre of free ammonia.

The Honigmann apparatus (shown in Fig. 23) consists of three or more conical vessels fitted with cooling pipes, which are filled with ammoniacal brine, and through which the carbon dioxide is pumped in series. The gas pipes and valves on these vessels are so arranged that the gas may travel after the manner of the counter-currents, *i.e.*, the strongest gas passes first through the vessel containing liquor weakest in free ammonia, whilst the almost spent gas travels through the liquor strongest in free ammonia.

At intervals, when precipitation of the sodium bicarbonate is complete, the contents of one of the Honigmann carbonators is blown to the filter, after which the vessel is refilled with ammoniacal brine and the process repeated.

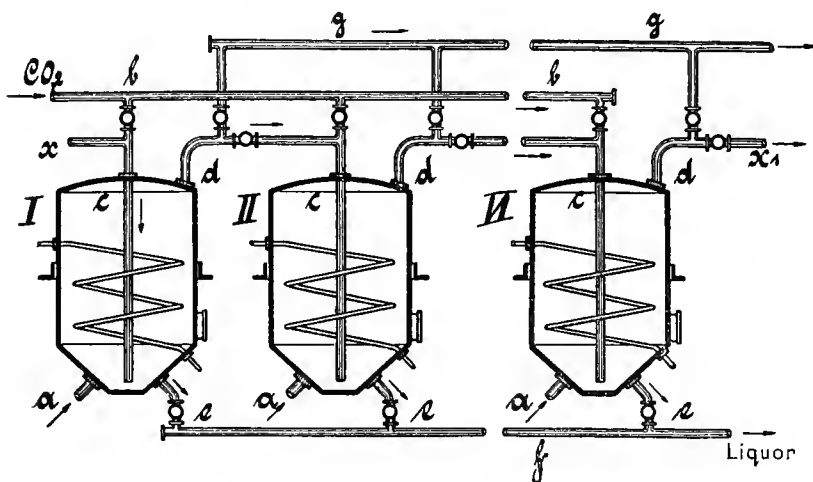


FIG. 23.—Honigmann's Carbonating Apparatus.

According to the size of the vessels the amount of bicarbonate of soda produced in one operation will vary from 8-12 tons. The time necessary for the production of this quantity depends, of course, on the concentration of carbon dioxide in the gas, together with the rate at which it is pumped through and absorbed. For the most part in practice the time occupied in carbonating the contents of one of the Honigmann vessels will be from six to nine hours.

The chief advantage claimed for the Honigmann apparatus is that the vessel does not become crusted up with bicarbonate of soda as is the case with the Solvay tower. Further, the resistance presented to the passage of the gas from the compressing engines is less, and in consequence a saving in fuel is effected.

The Honigmann apparatus, however, introduces an intermittently working plant into the middle of a process otherwise continuous; moreover, the system of counter-currents produced by the Honigmann apparatus is by no means so perfect as that produced by the Solvay tower, with the consequence that the absorption efficiency is not so great.

Thus with the Honigmann apparatus 80-90 per cent. of the total carbon dioxide passed through will be absorbed, whilst with Solvay towers the absorption efficiency may rise as high as 90-95 per cent.

When working with the Honigmann apparatus one vessel will always be discharging its contents to the filter whilst another is being filled, so that through these two vessels the carbon dioxide will

only be passing through a small head of liquor, and the absorption of carbon dioxide absorbed will not be so efficient as would otherwise be the case. During the period elapsing between the emptying of one carbonator and the filling of another the vessel will be completely empty, and absorption of carbon dioxide will then only be proceeding in the other two vessels. These defects do not appear in the Solvay tower, since with normal working the tower is always full of liquor.

On the content of carbon dioxide in the gas entering the carbonating plant the success of the whole process largely depends. The progress of the absorption of the carbon dioxide by the liquor is represented by the curves shown in Fig. 24.

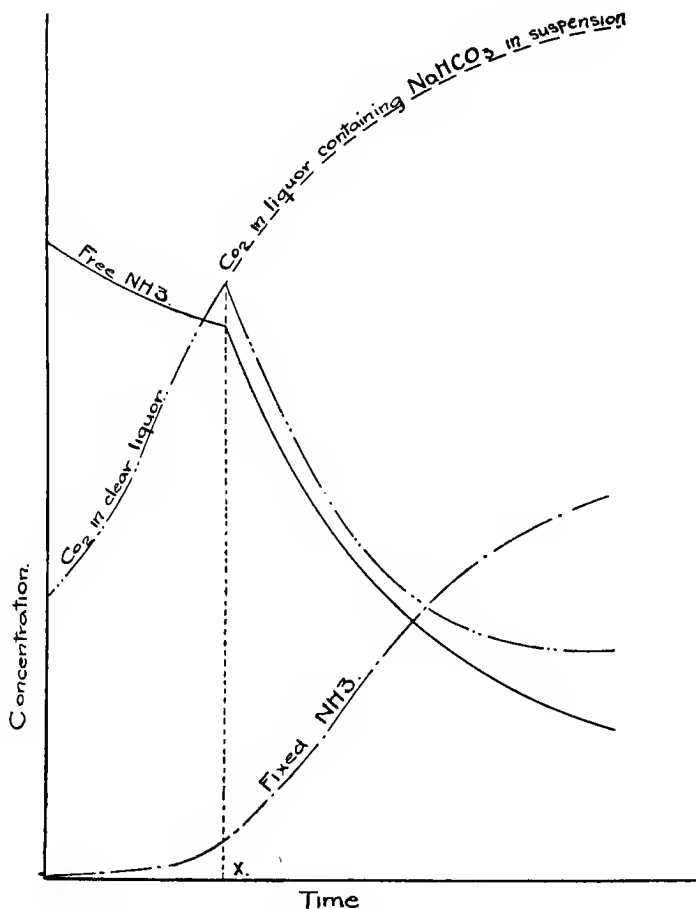
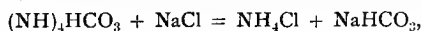


FIG. 24.—Absorption of CO_2 by Ammoniacal Brine.

It will be seen that the concentration of the carbon dioxide in the clear liquor continuously increases to the point x , when, owing to the separation of sodium bicarbonate at this time, a sudden fall occurs. The free ammonia content of the liquor falls slowly up to the point x owing to the removal of ammonia in the gas current, whilst after the point x the progress of the action,



is seen by a rapid fall of the free ammonia content, and a subsequent increase in the content of fixed NH_3 . At the time x the whole of the ammonia in the ammoniacal brine has been converted into the normal carbonate, and as has already been mentioned, where Solvay towers are used this part of the operation would be conducted in the semi-carbonating tower, whilst the finishing process from x onwards would be conducted in the "making" or "finishing" tower. A glance at the

curve shows that the preliminary carbonating process represents about one-third of the whole operation.

The design of the Solvay towers and Honigmann carbonators is based on a consideration of the work which must be done in order to absorb unit weight of carbon dioxide in ammoniacal brine of suitable concentration.

Thus in the case of the Solvay tower, the higher the column of liquor through which the gas has to pass, the more perfect will be the absorption, but, at the same time, the greater will be the work which must be done by the compressing engines to effect that absorption. Experiments carried out by the author show, as would be expected, that there is a certain point of maximum efficiency when a compressor of given capacity is under consideration.

If the work required to absorb unit weight of carbon dioxide is plotted against the height of liquor in the tower, all other conditions being constant, then a curve showing a minimum value is obtained.

The liquor blown by the gas pressure from the Solvay tower or from one of the Honigmann vessels has now to be filtered. The filtering plant originally consisted of a round or rectangular vessel provided with a false bottom, over which sacking or other similar material would be stretched. The magma of bicarbonate of soda and liquor was introduced into the vessel, when the liquor

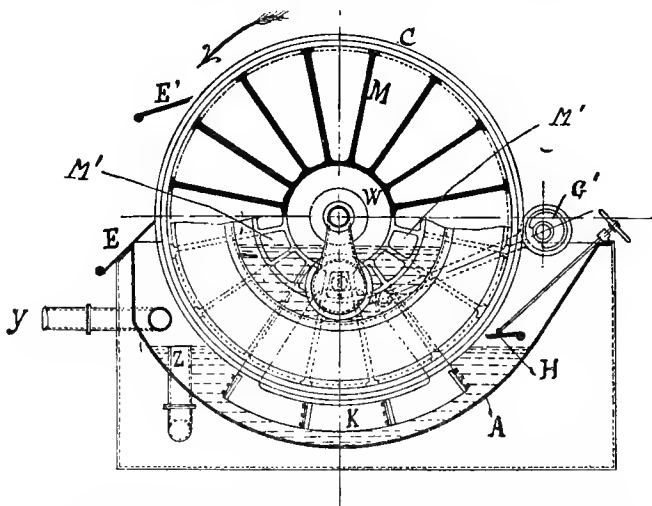


FIG. 25.—Mechanical Bicarbonate of Soda Filter—Revolving Cylinder Type

would pass through the false bottom, leaving the bicarbonate of soda to be subsequently washed with water. The filtering action would be assisted by a pump which, besides drawing off the liquor, maintained a vacuum under the cloth. The bicarbonate of soda was subsequently dug out, and in some cases it would be further dried in a hydro-extractor.

These old static filters are now quite obsolete. They have been replaced in all modern works by mechanical filters which consist of a rotating perforated drum or cylinder covered with flannel, inside of which a vacuum is maintained. The drum or cylinder is partially immersed in a trough containing the magma of bicarbonate of soda and liquor. By means of the pressure of the atmosphere the liquor is forced through the cloth, leaving on it a layer of the substance in suspension. As the drum or cylinder revolves the layer of bicarbonate of soda is washed with water, and subsequently scraped off by a knife. See Figs. 25 and 26.

When working with a mechanical filter, as described above, it was found that after a short time the pores of the filter cloth became clogged, and thus impeded the filtering process, with the consequence that from time to time the apparatus had to be stopped and the cloth washed. In order to avoid this trouble the filters are now divided into compartments, a vacuum being maintained in each

compartment, except the one which has just passed the knife and is about to enter the liquor. Into this compartment, by means of a mechanical device, a pressure of air or liquor is introduced. In this way the cloth is cleaned before it enters the liquor, with the consequence that the efficiency of the filter is maintained at a maximum.

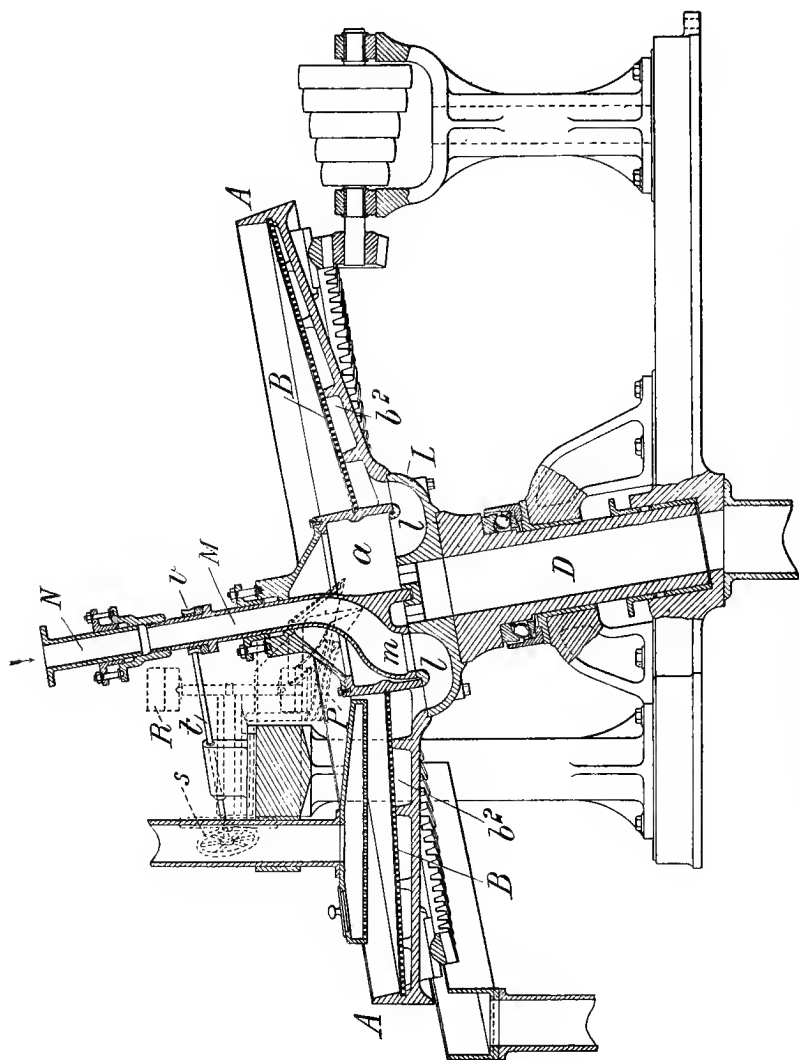


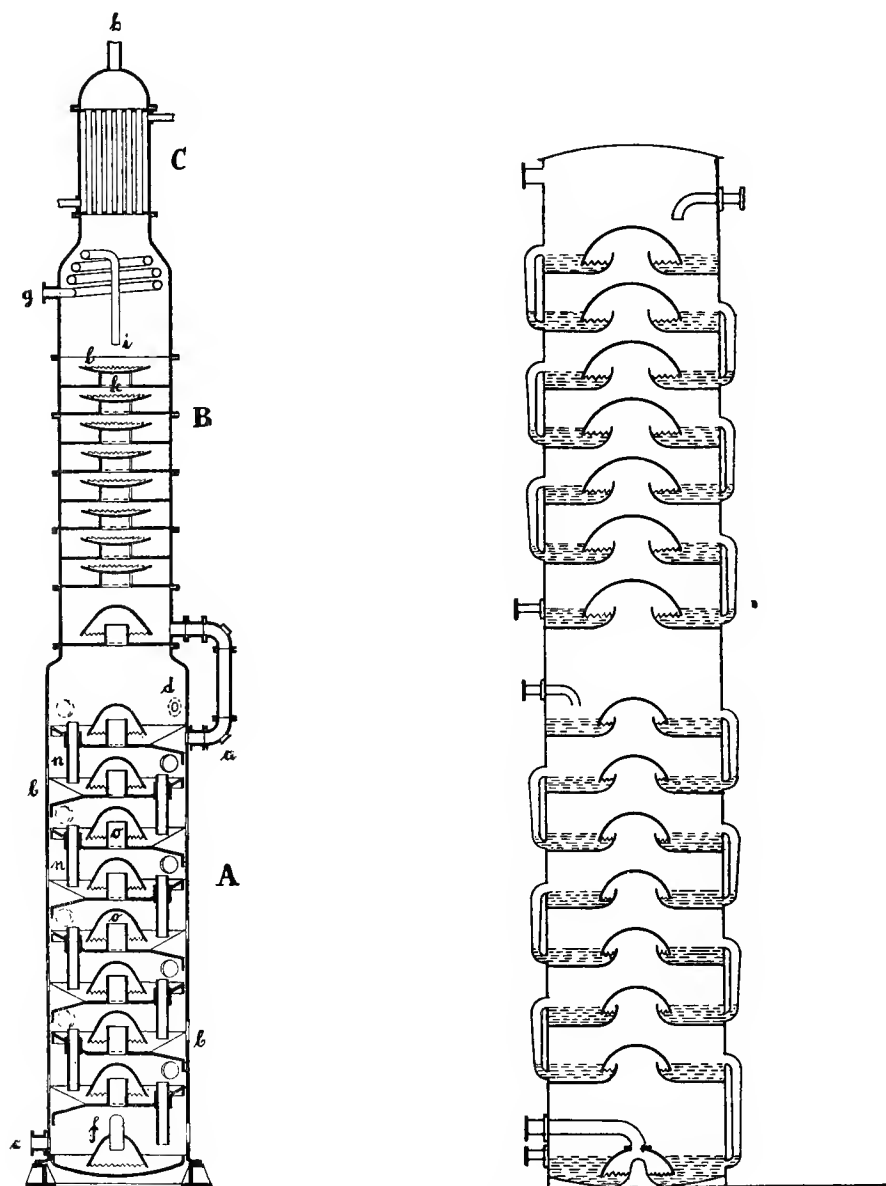
FIG. 26.—Mechanical Bicarbonate of Soda Filter—Rotating Drum Type.

These filters, which are described in English Patent 4,725, 1896, Solvay et Cie, also English Patent 28,791, 1903, Houghton and United Alkali Co., are shown in Figs. 25 and 26 respectively. Fig. 25 shows a filter of the revolving cylinder type, whilst Fig. 26 shows a filter of the rotating drum type.

The bicarbonate of soda leaving the filter will have the following composition :—

NaHCO_3	84	per cent.
H_2O	15	"
NaCl	0.3	"
NH_3	0.7	"

The mother liquor is diluted to an extent of about 10 per cent. by the wash water, and by dissolution in this water a small quantity of the bicarbonate of soda is carried into the mother liquor. This liquor now contains nearly the whole of the

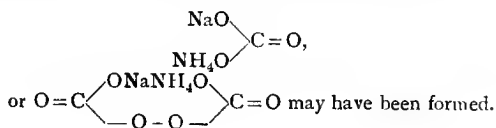


FIGS. 27 and 28.—Ammonia Distillers.

ammonia originally present in the ammoniacal brine. About 8 per cent. has been mechanically carried away by the passage of the gas, and will have been recovered by means of brine in the carbonator washer, and thence returned to the absorber.

A small quantity is contained in the bicarbonate of soda.

It appears quite impossible to remove by washing with water the last traces of ammonia present in the bicarbonate of soda. Whether the ammonium compound is present in the form of a solid solution, or has been absorbed by the sodium bicarbonate, it is difficult to say. Further, it is impossible to tell by analytical methods in what state of combination the ammonia is present. Probably a portion is present as ammonium bicarbonate, although it is possible that some compound such as a double or complex carbonate of sodium and ammonium as—

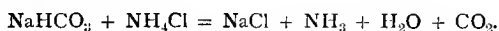


Distillation of the Ammoniacal Liquors

The mother liquor has now to be treated with steam and lime in order that the ammonia contained therein may be expelled and again absorbed in brine.

The ammonia distilling plant is perhaps the most important part of an ammonia soda factory, as it represents the connecting link between one cycle of operations and another.

The method of distilling the ammoniacal liquor consists in submitting it first to the action of steam when the free ammonia present, chiefly as the acid carbonate, is expelled. Here also any sodium bicarbonate present in the liquor reacts with the ammonium chloride thus :—



After the removal of the free ammonia the liquor is treated with milk of lime, and again subjected as before to a current of steam.

Two types of distilling apparatus are shown in Figs. 27 and 28.

The principle involved in all ammonia distillers is the same, although the construction of the apparatus varies somewhat in detail.

The liquor is pumped first of all into the top portion of the distiller known as the heater. A current of steam rising upwards expels the free ammonia. The liquor leaving the heater may now pass into the first compartment of that portion of the apparatus where the fixed ammonia is to be expelled. From here, after treatment with milk of lime, it flows downwards through the various compartments whilst the steam is bubbling through it, carrying away the ammonia gas. Thus as the liquor falls down the distiller, it becomes weaker and weaker in ammonia, until finally, on arriving at the last compartment when the whole of the ammonia has been driven off, the spent liquor is blown away by the steam pressure as the effluent.

In some cases the liquor leaving the heater may be treated with milk of lime in a special vessel. From this vessel it may either be blown or pumped back to the distiller, or alternatively the mixer may be placed at such a level that the liquor flows in and out by gravity.

The principles to be considered in the distillation of ammoniacal liquors are as follows :—

1. A system of counter-currents must be employed with regard to the transference of heat, in order that the efficiency of the heat exchange between steam and liquor may be a maximum. This it will be seen is more or less accomplished. The fresh steam comes into contact with the hottest liquor, whilst the exhausted steam at the top of the heater comes into contact with the coldest liquor.

2. A system of counter-currents must be maintained with regard to the concentration of the ammonia in the vapour and in liquid phases, or rather with regard to the tension of the ammonia in the vapour and liquid phases. By this, of course, it is meant that the fresh steam must come into contact with the liquor weakest in ammonia, whilst the exhausted steam must come into contact with liquors containing a high concentration of ammonia. This system of counter-currents here outlined is unfortunately not perfect, since, as will be shown later, it is impossible to produce a system of counter-currents perfect both as regards heat transference and ammonia expulsion.

The determining factor in the transference of the ammonia from the liquid to the gaseous phase will be the difference between the partial pressure of the ammonia in the liquor and vapour

respectively. Thus the ideal system for ammonia distillation would be a system where the tension of ammonia in the vapour increases as the tension of ammonia in the liquor increases. It may be represented as in Fig. 29.

The curves show that here, as we pass up the apparatus, the tension of the ammonia in the liquor and in the vapour steadily rise and converge until finally on leaving the apparatus they coincide alternatively; it may be said that the difference between the tension of ammonia in the gas and in the liquor increases from zero and then decreases again to that value. The velocity with which the ammonia is being expelled at any point will be proportional to the difference in the two partial pressures. Thus for example at the point x in the apparatus it would be proportional to the distance $A B$.

The actual conditions existing in a distiller deviate from the ideal conditions, owing to the fact that the tension of NH_3 in the liquor is at a maximum in the middle and not at the top of the column. This feature is shown in Fig. 30.

The point x indicates that compartment of the distiller where the lime is introduced. It will

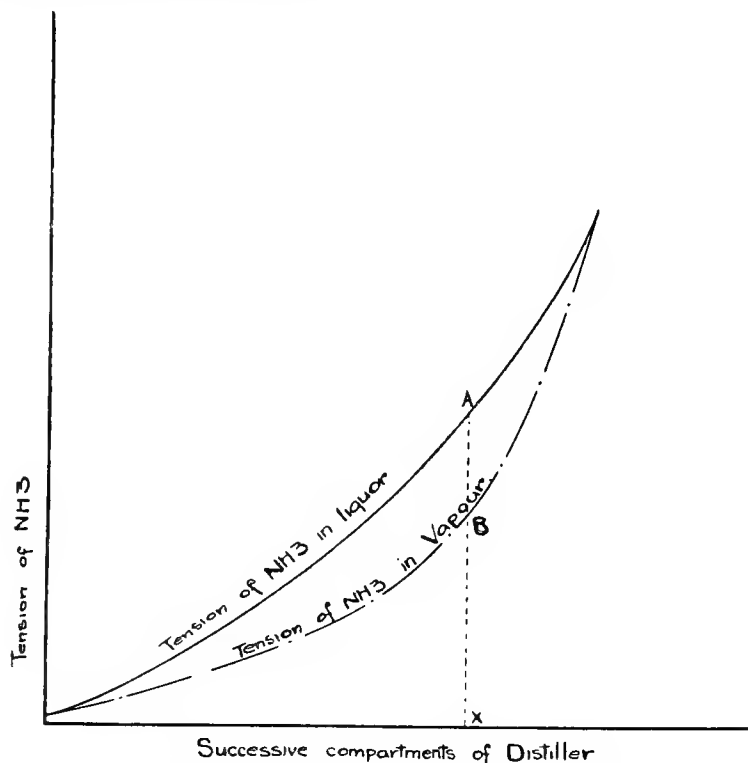


FIG. 29.—Ideal Conditions for Ammonia Distillation.

he observed that a very rapid increase in the tension of ammonia both in the liquor and vapour takes place at this point.

It is, of course, obvious that only so long as the partial pressure of the ammonia in the liquor exceeds the partial pressure of the ammonia in the vapour will the gas be expelled from solution. Since the tension of the ammonia in the liquor increases rapidly with rise in temperature, it may so happen that at the top of the heater where the coldest liquor is being introduced, the conditions will be reversed, *i.e.*, the tension of ammonia in the vapour exceeds the tension in the liquor, with the consequence that the concentration of the gas in the liquor will increase by the ammonia going into solution. These conditions are shown in Fig. 31. Thus at the point y the ammonia previously expelled starts to dissolve again.

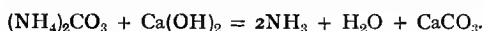
The tension of ammonia in the vapour after the point y will tend to decrease owing to the removal of ammonia from the vapour to the liquor, but at the same time the condensation of water vapour will lead to an increase in the tension of ammonia in the vapour, with the consequence that a break in the curve occurs at this point.

This condition of affairs is by no means hypothetical. In fact with an inefficient heater it may so happen that no free ammonia at all is evolved in this part of the apparatus; in fact it is quite

possible, under very adverse conditions, which, however, sometimes exist, that the liquor leaving the heater contains a higher concentration of ammonia than when it entered.

The dotted line in Fig. 31 shows how this might result. It will be observed that in this case the tension of the ammonia in the liquor never in the heater exceeds the tension of ammonia in the vapour.

Under these conditions, which are of course exceedingly objectionable, it will usually be found that the liquor leaving the heater contains a large quantity of carbon dioxide present as ammonium carbonate, with the result that the milk of lime combines with the carbon dioxide to give calcium carbonate—



Hence not only carbon dioxide but also lime is wasted, since the reaction—

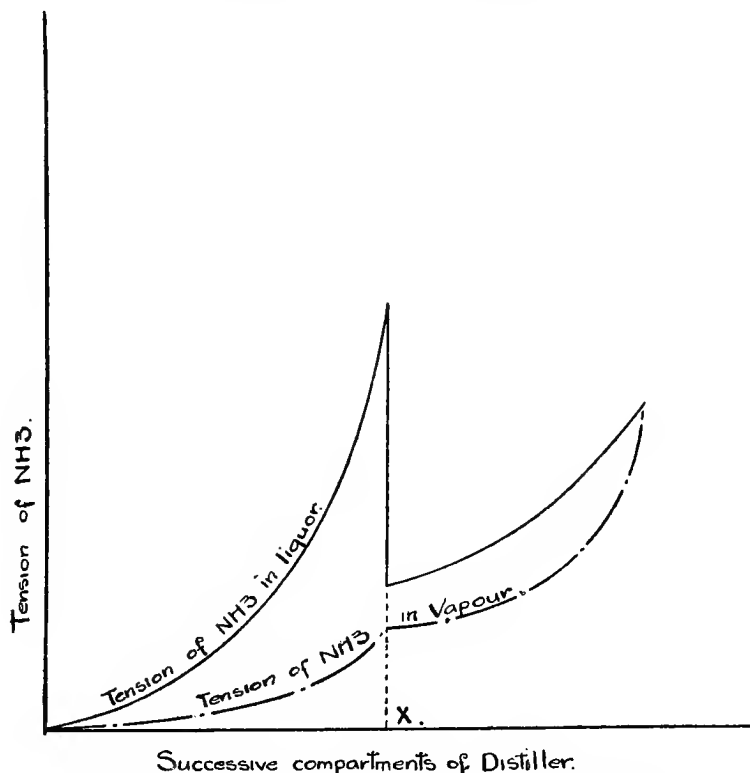


FIG. 30.—Tension of NH_3 in Liquor during Process of Distillation.

only proceeds very slowly in the still and the greater part of the calcium carbonate will pass away as such.

The distillation of ammonia in the upper portions of the still proceeds with great rapidity, but the final expulsion of the lost traces of ammonia is only accomplished with difficulty.

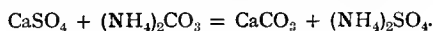
In order that there may be no loss of ammonia in the effluent, it is necessary to work with a small excess of lime in the distiller. This excess must, of course, be kept as low as possible, and with an efficient plant skilfully handled will vary from 3.5 g. per litre.

It will be apparent from a consideration of the factors previously outlined, on which the distillation of the ammoniacal liquor depends, that it will be especially advantageous to work the distiller under a vacuum, since in this way the partial pressure of the ammonia in the vapour is decreased, and the tendency for the gas to be expelled from solution is, of course, much greater. All modern distillers are now worked under a vacuum which extends through the absorber and washing towers. Care has to be taken in working the apparatus under a vacuum that the various compartments in the distiller do not become gas locked, otherwise the liquor will "hold up" in the

heater, and thereby cause great irregularities in the working of the entire plant. With a distiller suitably designed and worked under the correct conditions, this gas locking trouble, however, does not occur.

The construction of ammonia distillers has been continuously improved and their capacity increased until at the present day one unit will distil sufficient liquor to produce from 1,000 to 2,000 tons of ash per week, working with absolute regularity for twelve months, when supplied continuously with steam, liquor, and milk of lime. A certain quantity of scale slowly forms in the distiller; it consists for the most part of calcium sulphate and Na_2SO_4 which has been produced by the following reactions from the calcium sulphate originally present in the brine.

In the absorber—



In the distiller—

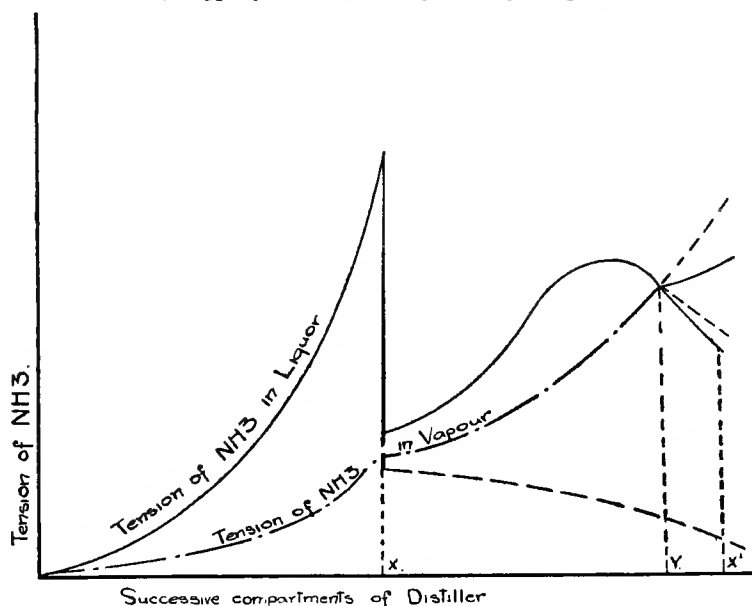
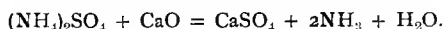


FIG. 31.—Tension of NH_3 in Liquor during Process of Distillation, showing Absorption of NH_3 previously expelled.

A sample of this scale examined by the author had the composition :—

CaSO_4	76.83 per cent.
CaCO_3	6.35 "
Na_2SO_4	3.76 "
MgSO_4	0.04 "
NaCl	0.48 "
H_2O (difference)	13.54 "

The steam used for driving off the ammonia in the distillers is supplied by the exhaust of the compressing and other engines in the plant. The valves on these engines will be set in such a way that expansion in the cylinder takes place down to the back pressure of the ammonia stills. In order that the steam consumption may be kept low, it is apparent that this back pressure must be reduced as far as possible. This is, of course, in part effected by working the distiller under a vacuum. **The total quantity of heat that must be supplied** to a distiller depends on a very large number of factors, so that it can hardly be here attempted to consider the question in detail. It will be sufficient to state that in practice it will approximate to 3,000,000 kilo calories per ton of ash produced.

In the design of a factory it is an important matter to decide as to how many of the engines will be made condensing and how many non-condensing in order that the requisite quantity of steam may be admitted to the ammonia distiller.

The economy obtained by exhaust steam is evident, the engines merely acting as reducing valves. Of the total heat supplied to the engine, 97 per cent. will pass away in the exhaust.

The utilisation of high pressure and superheated steam for the purpose of ammonia distillation has often been suggested. The fact is frequently lost sight of, however, that the effect of the superheat will be almost entirely removed in the bottom compartment of the distiller. The final result being that rather less effluent will be produced owing to the evaporation of a certain quantity of liquor in the bottom compartment. Further, it will already have been observed that the important factor in expelling the ammonia from solution is not so much the intensity of the temperature of the steam as the volume occupied by it, since each bubble rising through the apparatus has a tendency to become saturated with ammonia gas.

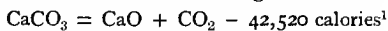
The gases leaving the distiller are maintained at a temperature of 75° - 85° C., and will in consequence be saturated with water vapour at this temperature. In order that the brine in the absorber may not be unduly diluted or heated by the condensation of the water vapour, the temperature of these gases is reduced to about 57° - 60° C. by passing through a cooler which may be of the evaporative or multitubular type.

The liquor condensing in these coolers is a strong solution of ammonia containing more or less carbon dioxide. It is run back to some portion of the heater, preferably the upper compartments, in order that the system of counter-currents may be maintained.

The gas, after being cooled, passes to the absorber, when the cycle of operations is once more commenced.

It is essential that the pipes carrying the ammonia gas be of ample dimensions in order that very little frictional resistance be offered to the passage of the gas current.

The Lime-Kilns.—The function performed by the lime-kilns in the ammonia soda process is two-fold. They supply not only most of the gas necessary for the carbonating operation, but also the lime for decomposing the ammonium chloride. Owing to the necessity for recovering the gas, the limestone is calcined directly with coke in closed kilns. The suitably proportioned mixture is introduced into the top of the kiln, where it is heated by the issuing gases. It then passes through the zone of combustion where the change



takes place.

The hot lime, as it passes further down the kiln, is cooled by the air entering and is finally discharged, either by mechanical means or by hand, into waggons.

It will be seen that an efficient kiln is perfectly regenerative in action, the whole of the heat being conserved.

Fig. 32 shows one type of kiln in use.

The lime may be delivered into a vessel provided with a perforated false bottom provided with agitating gear (shown in Fig. 33); here it is slacked by hot water. The milk of lime containing 250 g. per litre CaO is run off and sieved, when after passing through storage tanks it is delivered to the ammonia stills.

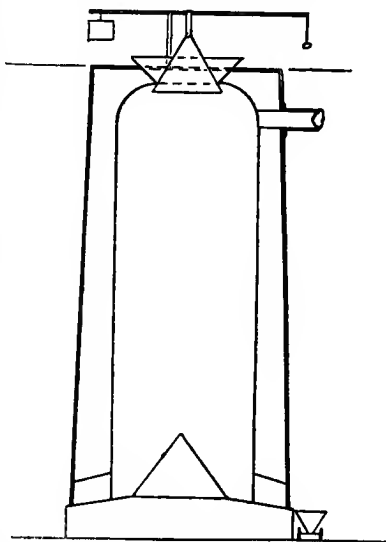


FIG. 32.—Lime-Kiln.

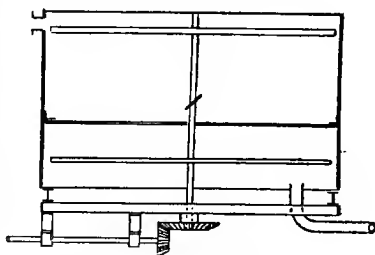


FIG. 33.—Lime Slacker.

¹ Thomsen.

These intermittent lime slackers have in some work given way to a continuous form of apparatus.

The **gas** evolved by the lime-kilns is drawn by the compressing engine through scrubbers which consist of towers, where the gas is either caused to bubble through layers of water, or it is exposed to the action of a current of water flowing over some suitable packing material, such as coke, limestone, blue bricks, etc. After passing through the scrubbers it is mixed with the gas given off during the decomposition of the bicarbonate of soda, and delivered by the compressors to the carbonating plant.

Calcination of the Bicarbonate of Soda.—Having now described the cycle of operations which has led to the formation of sodium bicarbonate, and

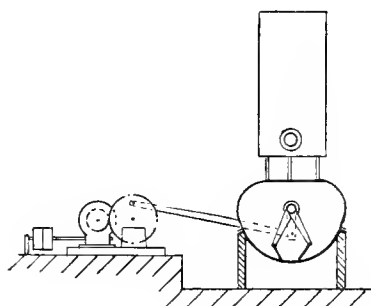
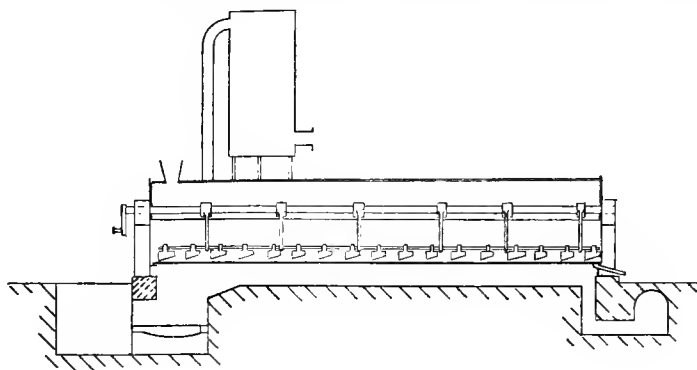


FIG. 34.—Thelen Pan.

subsequently to the recovery of ammonia from the mother liquors, we may now proceed to the final stage of the operation—the conversion of the bicarbonate of soda into the normal carbonate. The decomposition is effected in one or two operations, and may be carried out in mechanical or static furnaces.

When the operation is carried out in two stages the bicarbonate of soda is first calcined to the point when most of the moisture and the whole of the ammonia has been evolved. It is then passed to the Thelen pans where the decomposition is completed.

The final calcining operation may also be carried out in a revolving furnace, such as that described in United States, America, Patent 386,664, 1888, which is 60 ft. long, 5 ft. diameter, and is heated externally by gas.

The most usual form of calcining furnace is that known as the **Thelen pan**, which is shown in Fig. 34.

It consists of a number of cast-iron semicircular plates about 2 in. thick, 6-10 ft. in diameter, and 7-8 ft. long. A number of these pans are bolted together by means of flanges, so that the total length of the furnace may be from 30-50 ft.

The pans are heated externally by means of gas, or coal. The flue gases traverse the length of the furnace and pass away by means of a downtake.

The moist or partially dried bicarbonate of soda is fed by a mechanical device into the furnace in such a way that no gas can escape. The material inside the furnace is carried backwards and forwards by a number of scrapers so inclined as at the same time to push the material forward. These scrapers are attached by means of arms to a rotating shaft which makes a semicircular movement. In this way the substance is pushed slowly over the pans towards the end of the furnace and is eventually discharged at a temperature of about 160° C. The discharge of the material is conducted in such a manner as to prevent the entrance of air or the escape of gas.

The mechanical gear on these furnaces will, according to the size of the apparatus, absorb from 10-20 H.P.

The following figures, taken by the author, show the progress of the calcining operation as conducted in a Thelen pan, the samples being taken every six minutes. The bicarbonate of soda was a special sample arranged to contain as near as possible 20 per cent. of moisture.

Na_2CO_3 per Cent.	NaHCO_3 per Cent.	NaCl per Cent.	NH_3 per Cent.	H_2O per Cent.
<i>Nil.</i>	79.0	0.57	0.75	19.68
33.08	56.0	1.0	0.12	9.8
35.84	54	1.07	0.09	9.0
88.27	9.0	1.0	0.03	1.7
88.5	9.0	1.0	<i>Nil.</i>	1.5
99.0	<i>Nil.</i>	1.0	<i>Nil.</i>	<i>Nil.</i>

The mixture of steam, ammonia, and carbon dioxide leaving the furnace is drawn first of all through a multitubular condenser. Here the steam is condensed, giving a solution, the composition of which will vary within small limits according to the content in ammonia and moisture of the material which is being calcined. It will contain, however, about 25 g. per litre of ammonia and 42 g. per litre of CO_2 , and is thus a mixture of the normal and acid carbonate of ammonia. After leaving the condenser the gas may be passed through a brine or water scrubber, where the last traces of ammonia will be recovered. Finally after mixing with the furnace gas it passes to the compressors.

Although it has been shown by **Gautier** (*Ber. Deutsch. Chem. Ges.*, 9, 1434, 1876) that complete decomposition of sodium bicarbonate takes place readily at 100°-110° C., yet in practice in order to increase the velocity of the action much higher temperatures are used, and in the hottest part of the furnace under the Thelen pans the temperature will be in the neighbourhood of 1,000° C. The presence of moisture in the material, its low conductivity for heat, together with the tendency which the crude bicarbonate has to form into lumps, renders this part of the process most difficult to carry out economically in practice.

In order to calcine 100 kilos of bicarbonate of soda, the following quantities of heat must be supplied :—

Decomposition of NaHCO_3	27,800 calories.
Evaporation of water	18,900 "
Heat lost by the CO_2 -	1,610 "
Heat carried away in ash	4,500 "
Radiation, etc.	13,000 "
	<hr/> 66,000 approx.

Assuming coal with a calorific value of 6,500 calories is used and a heat efficiency of 70 per cent. in the furnace, the quantity of coal required will be about 14.5 kilos per 100 kilos of ash, *i.e.*, the amount of fuel burnt under the furnaces will be 14½ tons for every 100 tons of ash produced.

When the soda ash is intended for export or glass-making purposes, it is after leaving the Thelen pans again calcined at a high temperature in a Mactear furnace, and subsequently ground to a powder. In this way the density is considerably increased. Thus, whereas 100 g. of light ammonia ash occupies a space of about 600-700 c.c., the same quantity of "heavy ash" only occupies about 300 c.c.

The soda ash is conveyed by a worm conveyor to the ash mill, where in a mechanical sieve it is reduced to a fine powder, and is then ready for packing.

The Compressing Engines.—The gas compressors form a very important part in an ammonia soda factory. Their function is, of course, after drawing the gas from the lime-kilns and the furnaces to force it through the carbonating apparatus. The back pressure exerted by the carbonating apparatus will be from 35-40 lbs. with Solvay towers, and from 30-40 lbs. per square inch when Honigmann's carbonators are used.

The compressors are direct acting, and are usually fitted with mechanically operated valves such as those of the Burchardt or Riedler type. It is impossible to use the highest class of valve giving a sharp cut off, owing to the exceptional difficulty of removing the last traces of dust from the lime-kiln gases. It is of course essential that in any case the gas passing to the engines should be as free as possible from suspended matter, otherwise the gas cylinders and valve faces rapidly become scored. The cylinder will in all cases be water-jacketed. It is necessary, however, to cool the gas still further before it enters the carbonating plant.

Content of Carbon Dioxide in the Various Gases.—A very large portion of the power raised in an ammonia soda factory will be used in pumping the carbon dioxide through the carbonating plant. It is hence a matter of the very greatest importance to maintain the content of carbon dioxide in the gas as high as possible in order that energy may not be uselessly expended in compressing large volumes of weak gas.

In order to produce 1 metric ton of sodium carbonate the quantity of carbon dioxide theoretically required is 422 cub. m. at N.T.P.

A certain quantity of carbon dioxide will, however, after compressing be lost owing to the following causes:—

1. Inefficient absorption in the carbonating plant.
2. Formation of calcium carbonate from calcium sulphate in the brine.
3. Incomplete expulsion of carbon dioxide in the heater.
4. Incomplete absorption of carbon dioxide in the absorber.
5. Leakage through valves, piston rod, glands, etc.

The total loss of carbon dioxide will vary in different factories between fairly wide limits, and it will usually be found necessary to pump from 450-500 cub. m. per metric ton of ash produced.

Of the total quantity of carbon dioxide required for the production of the sodium carbonate, theoretically 50 per cent. should be drawn from the soda calciners, and 50 per cent. from the lime-kilns. Since, however, the quantity of gas that has to be passed exceeds the theoretical quantity, the greater volume must be drawn from the lime-kilns, since the calcination of the bicarbonate of soda cannot furnish a greater quantity than 211 cub. m. per ton of ash produced.

The Content of Carbon Dioxide in the Lime-Kiln Gas.—In order to calcine 100 kilos of limestone, the following quantities of heat must, in practice, be supplied:—

Decomposition of CaCO_3 -	-	42,500 calories.
Loss by withdrawal of hot lime, exit of hot gases, radiation, etc.		15,100 "
	Total	<u>57,600</u> "

Now the quantity of heat given out by the burning of 1 kg. of carbon present in the coke will be approximately 8,000 kilo calories. The total quantity of carbon necessary is hence:—

$$\frac{57,600}{8,000} = 7.2 \text{ kg.}$$

This quantity of carbon will require for combustion 13 cub. m. of oxygen yielding 13.0 cub. m. of CO_2 . As the oxygen is supplied by the air there will also be present 53.6 cub. m. of nitrogen.

Thus the issuing gases will have the following composition :—

CO ₂ from decomposition of CaCO ₃	22.4 cub. m.
CO ₂ from combustion of coke -	13.4 „
N ₂ from atmosphere	53.6 „
	<hr/> 89.4 „

and the content of the carbon dioxide in the gas will be

$$35.8 \times \frac{100}{89.4} = \text{approximately } 40 \text{ per cent.}$$

Assuming coke with a content of 90 per cent. available carbon is used, the consumption of this material will be

$$7.2 \times \frac{100}{90} = 8.0 \text{ kilos per } 100 \text{ kilos of limestone.}$$

Content of Carbon Dioxide in the Furnace Gases.—The design of the calcining furnaces has been continuously improved until the gas now drawn from this source contains from 90-98 per cent. of carbon dioxide, and practically no loss occurs.

Content of Carbon Dioxide in the Mixed Gas.—If it is assumed that the total loss of carbon dioxide in the process, owing to the various causes previously mentioned, is 10 per cent., then it will be necessary to pump $422 \times \frac{100}{90} = 469$ cub. m. of carbon dioxide to produce 1 metric ton of ash.

Of this quantity the furnaces should supply 200 cub. m., leaving $469 - 200 = 269$ cub. m. of carbon dioxide to be supplied by the kilns.

200 cub. m. of carbon dioxide from furnaces at 95 per cent.	= 210 cub. m. gas.
269 „ „ „ „ lime-kilns at 40 per cent.	= 672 „

Total 882

Thus in order to produce 1 metric ton of ash it will be necessary to compress 882 cub. m. of gas containing 469 cub. m. of carbon dioxide, or 53.2 per cent. by volume.

It will be seen that the content of carbon dioxide in the mixed gas is not only dependent on the strength of the lime-kiln and furnace gases, but also on the total quantity of gas pumped, and on the quantity of gas recovered from the furnaces.

Summary of the Operations.—Fig. 35 shows diagrammatically the manner in which the various parts of the apparatus in the ammonia soda process are combined together.

Limestone mixed with coke is charged into the kiln A. The issuing mixture of carbon dioxide and nitrogen is drawn by the compressing engines C through the water scrubber B, and is then pumped through the carbonating tower D, where it meets a stream of ammoniacal brine. Here most of the carbon dioxide is absorbed, and the spent gas containing a small quantity of ammonia passes through the brine washer N where the ammonia is recovered. A final scrubber O, fed with water, removes the last trace of ammonia gas should any escape the washer N.

The magma of bicarbonate of soda and ammoniacal liquor is blown from the tower D by means of the pipe K to the filter P. The moist sodium bicarbonate passes to the furnace T, where it is calcined and subsequently discharged as soda ash at G.

The gas leaving the furnace is drawn by the compressor C through the condenser S, where the water vapour is condensed. The final traces of ammonia in the gas are removed in the washer Q, after which it is mixed with the lime-kiln gas.

The liquor leaving the filter passes to the storage tank Q, and is delivered by the pump R to the top of the heater L of the ammonia distiller. The ammonia is expelled from solution by a current of steam supplied through the pipe A. After reaching the bottom of the heater L the liquor leaves by the pipe D, is mixed with milk of lime, and returned at C, when the fixed ammonia is expelled in the still K. The spent liquor is blown away by the pipe B.

The gas leaving the ammonia distiller, after being cooled in the apparatus H, bubbles through brine in the absorber G, where most of the ammonia is dissolved. Any gas not absorbed passes to the washer M, where, by means of fresh brine, the last traces of ammonia are removed. The brine entering the absorber comes from the tank V after passing through the washers N and M.

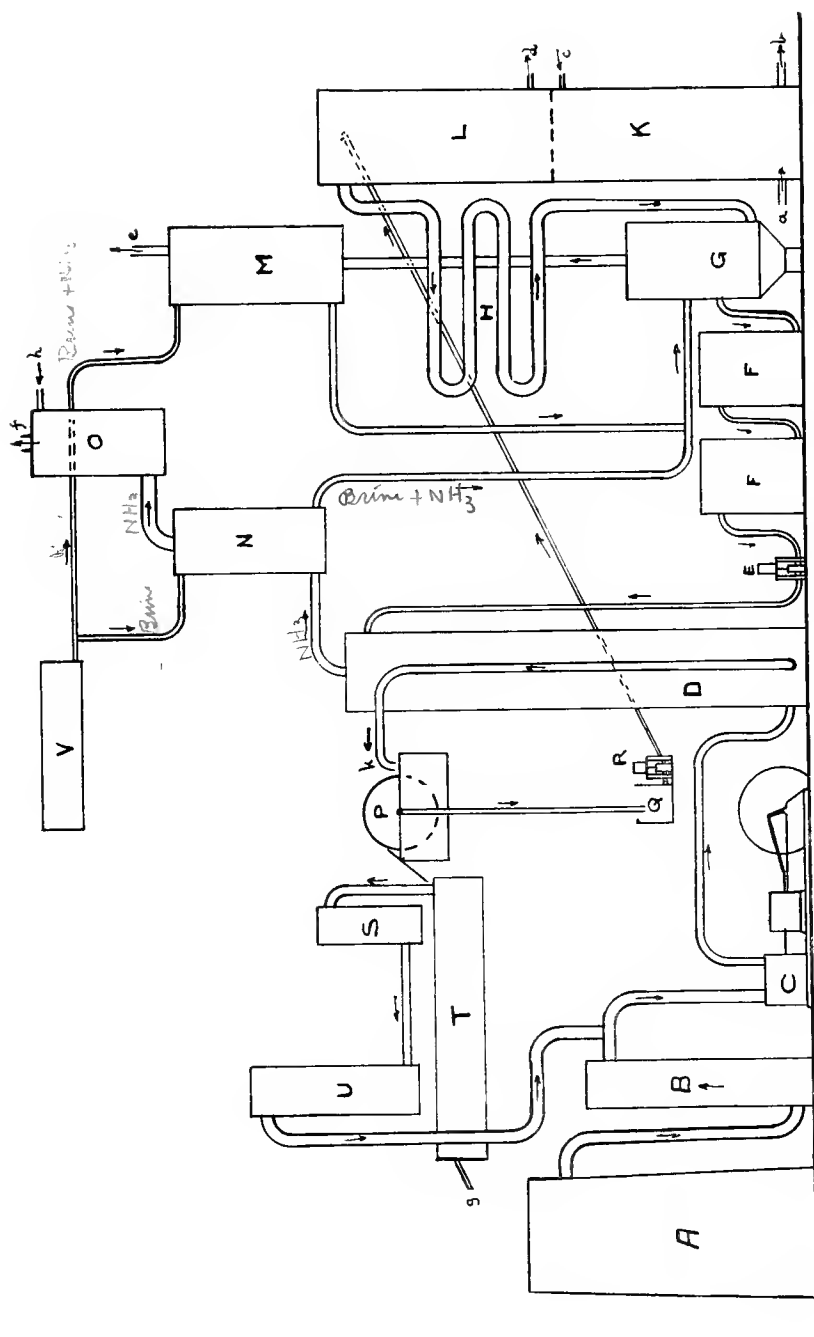


FIG. 35. — Diagram showing Ammonia Soda Process in Outline

The ammoniacal brine, leaving the absorber G, passes through the settling vats F and F, and is delivered by means of the pump E to the top of the carbonating tower.

Control of the Process.—In order that the final product may be produced with the minimum consumption of raw materials, and in order that the maximum output of the various units may be maintained, it is necessary to watch every phase of the process with the greatest care.

The lime-kiln gases and furnace gases will be continuously sampled in order that the concentration of carbon dioxide may be maintained at a maximum. Further, the relative quantities of each of these gases, as shown by the mixed gas test, will be watched.

This relation is readily obtained.

Let x = volume of lime-kiln gas, and p = per cent. of CO_2 ,

y = volume of furnace gas and p_1 = per cent. of CO_2 ,

P = per cent. of CO_2 in mixed gas.

The $\frac{px}{100}$ = volume of CO_2 in lime-kiln gases,

and $\frac{p_1y}{100}$ = volume of CO_2 in furnace gas.

Hence,
$$\frac{\frac{px}{100} + \frac{p_1y}{100}}{x + y} \times 100 = P,$$

or, $y(p_1 - P) = x(P - p),$

i.e., $x : y = p_1 - P : P - p.$

It will be seen that relative volumes of lime-kiln and furnace gas are inversely proportional to the amounts by which the respective carbon dioxide content differs from the mixed gas content of carbon dioxide, and the relative volumes of carbon dioxide supplied can be obtained thus :—

$$\frac{\text{CO}_2 \text{ from lime-kilns}}{\text{CO}_2 \text{ from furnaces}} = \frac{p(p_1 - P)}{p_1(P - p)}.$$

This expression, $\frac{p(p_1 - P)}{p_1(P - p)}$, should approach unity.

The smaller the value is, the higher will be the efficiency of the process.

The spent gases leaving the carbonator washer must also be analysed in order that this loss of carbon dioxide may be kept as low as possible.

It may be here pointed out that if the gas leaving the process contains 5 per cent. of carbon dioxide, the percentage of carbon dioxide really lost is much greater. If x = per cent. of CO_2 in original gas, and y = per cent. of CO_2 in the gas leaving the process, then the percentage loss of CO_2 will be—

$$\frac{(100 - x)}{(100 - y)x} \times 100,$$

from which expression it is apparent that the percentage loss of carbon dioxide is dependent, not only on the actual percentage of carbon dioxide in the gas going to the atmosphere, but also on the percentage of carbon dioxide in the gas entering the process, for by increasing x the value of the above expression will be lower even if the value of y remain constant.

According to the efficiency of the carbonating plant, the exit gases will contain from 2-10 per cent. of carbon dioxide. An average of 3-4 per cent. will represent fairly good modern practice.

The ammoniacal brine in the absorber will be sampled every few minutes, and its content in ammonia and salt determined.

It is essential to the success of the process that the concentration of ammonia in the ammoniacal brine keep constant at the required figure, whilst the salt content must continually be kept as high as possible.

During the carbonating operation frequent samples are taken at various stages. Where a semi-carbonating tower is employed, the content of the carbon dioxide in the liquor leaving will be determined by Lunge's volumetric method. During the precipitation of the bicarbonate of soda the temperature is carefully controlled, and the decrease in the content of free ammonia watched. The operation is so conducted that the liquor passing to the filter is of uniform composition.

The bicarbonate of soda leaving the filter will be tested for ammonia, salt, and moisture. During the calcining operation the physical appearance of the material undergoing decomposition and temperature of the product leaving the furnace are the most important features to be watched. The final product may be tested for sodium carbonate, salt, insoluble matter, and iron. The quantity of the two latter constituents should be almost negligible, with the consequence that the soda ash produced is exceptionally pure, containing from 99.99.7 per cent. of Na_2CO_3 .

The return liquor going to the ammonia still is tested for free and fixed ammonia; the liquor leaving the heater for free ammonia and carbon dioxide.

The concentration of the milk of lime, and the lime excess after admixture with the ammoniacal liquor, require very careful control if the distilling operation is to be carried out with the minimum loss of lime and ammonia.

It is essential that the strength of the milk of lime be maintained as high as possible, in order to avoid excessive dilution of the liquors and consequent increase in the steam consumption in the still. Further, as every cubic metre of effluent will carry away from 2.10 kilos of lime and a trace of ammonia, it is apparent that the total volume of effluent must be kept low.

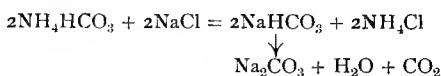
The content of ammonia present in the liquor nearing the bottom of the ammonia distiller is continuously determined, and the operation so conducted that the liquor in the last compartment contains an almost negligible quantity of ammonia.

In practice, however, this liquor will always contain a trace of ammonia, although the total amount should not exceed .001 g. per litre. The quantity of effluent passing per ton of ash produced will thus be carefully recorded.

The temperature of the gas at the top of the heater, and of the liquor leaving the heater, is kept under close observation. Too high a temperature at the top of the heater will mean excessive steam consumption, and a large amount of work being placed on the gas coolers. Too low a temperature will mean inefficient working of the heater. In consequence, the temperatures are maintained at the figure which experience has shown to be most suitable for the particular apparatus in question.

The temperature of the gas leaving the coolers must be maintained in the region of $58^\circ\text{--}60^\circ\text{C}$. Below this range the pipes will become blocked with ammonium carbonate. Above it excessive quantities of water vapour are carried to the absorber, and the salt content is diminished. Further, the temperature of the absorber will also rise, and this, as it has been mentioned, it is desirable to keep as low as possible.

The Yield of Soda Ash per ton of ammonia distilled is an important factor. The equation is:—



shows that 1 ton of ammonia should produce 3.1 tons of ash.

In practice, however, for a large number of reasons, the yield falls considerably short of this figure, and may fall as low as 1.6 tons of ash per ton of ammonia distilled.

In any plant when the stock of ammonia is more or less constant the determining factor in the output is a figure which may be called the **ammonia cycle**. This figure is obtained from the expression

$$\frac{\text{Tons of NH}_3 \text{ distilled per unit of time}}{\text{Tons of NH}_3 \text{ in stock}},$$

and thus represents the number of times the stock of ammonia has gone through the cycle of operations in the period under consideration. The greater the speed,

with which the ammonia stock can be circulated through the various stages of the operations, distilling, carbonating, and filtering, the greater, of course, is the production.

It is scarcely necessary to add that the power consumed in the ammonia soda process should be generated as economically as possible, the evaporative efficiency of the boiler plant being controlled in accordance with the most modern practice. With normal working the steam load will be practically constant. Large quantities of hot water for boiler feed purposes can usually be obtained from various sources, so that the efficiency of the boiler plant should be high. The effective utilisation of the steam once generated will depend on the efficiency of the process. A large proportion will be consumed by the compressing engines, and it is necessary to indicate frequently the gas and steam cylinders in order that their efficiency may be maintained at a maximum. Further, the relation between the quantity of gas which appears to have passed from chemical considerations, and that which should have been pumped, assuming a certain volumetric efficiency of the compressor, should be recorded in order that any discrepancy may at once be noticed.

Although the chemical reactions underlying the ammonia soda process are so simple in character, yet on the industrial scale the greatest difficulties are presented. The various operations are so interdependent one on the other that inefficient working, or a breakdown of any portion of the plant, is at once reflected throughout the entire process. Further, the disturbing influence will make itself felt for a considerable period after the defect has been remedied.

In order to maintain the continuity of operations so essential to the success of the process, it is necessary that those parts of the plant liable to accident or breakdown be duplicated.

The manufacture of ammonia soda in the most economical manner is an operation on which must be brought to bear experience, together with the highest technical ability.

In modern factories a very high state of efficiency has been arrived at, and with almost monotonous regularity, day and night for three hundred and sixty-five days of the year, many hundreds of tons of soda ash per week are produced with a minimum consumption of raw materials.

Factories designed, and subsequently worked, by those without previous experience in the industry have usually had to undergo many alterations before efficient working could be attained. Once, however, the initial difficulties of the process have been overcome, and the plant has been made efficient, very little further trouble will result.

Consumption of Raw Materials and Costs.—The raw materials used in the ammonia soda process are coal, coke, limestone, and ammonia.

The cost per ton of these materials will be governed partly by the locality of the factory, whilst the actual consumption will depend on the efficiency of the process.

Such has been the advance made in the industry, that the figures given by Schreib (*Chem. Zeit.*, 1894, p. 1951), as the lowest possible according to calculation, are those now realised in actual practice.

Consumption of materials for 100 kilos of soda :—

Coke	6.5 kilos.
Limestone	120 „
Coal	50 „
Ammonia	0.22 „

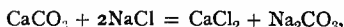
Whilst the consumption of coke will be slightly more than the figure given by Schreib, the ammonia loss will be considerably less, and with good practice should not exceed 0.1 kilo per 100 kilos of ash. In order to arrive at the final cost of production of the finished article, it will be necessary to add to the cost of raw materials, wages, standing charges, cost of package, etc. As these latter items are so variable, it will be unnecessary to discuss them here in detail. Owing to the great facilities usually afforded in the factory for handling the raw materials, and to the fact that the actual product during the various stages of manufacture is never touched by hand, the wages item will be very low, whilst owing to the large amount of plant and land necessary for producing ammonia soda, standing charges will be rather high.

Finally, it may be said that the ammonia soda process is in the hands of very few firms, and is by them conducted with the greatest secrecy, so that those details so essential to the commercial success of the process are not known to the general public.

Those who peruse the patent literature will have been struck in recent years by the absence of matter relating to this process, and from this might be led to conclude that little or no progress has recently been made. Such, however, is by no means the case. Rather than indicate to competitors the directions along which economy can be effected, and rather than invite them to infringe the patent in question, or to improve upon it, the manufacturer prefers to carry on his operations behind closed doors, behind which none but the most trusted employees are admitted.

Modifications of the Ammonia Soda Process

The final result of the ammonia soda process,



leads to the formation of two products, only one of which is of any great commercial value. In consequence of this, the application of the process to the treatment of **sodium sulphate** was patented by Bower, English Patent 8,413, 1840; Gerlach and Weldon, English Patent 5,605, 1883; also Gaskell and Hurter, English Patent 5,712, 1883. Its application to the **sodium nitrate** was patented by Lesage & Co. in 1871, and by Chance in 1885. Colson (*loc. cit.*), again, discusses this subject, which has been further investigated by Fedotieff and Koltunow (*Zeits. anorg. Chem.*, 1914, 85, 247). They find that the behaviour of sodium nitrate is very similar to that of sodium chloride, although it is possible by suitable treatment to precipitate the whole of the sodium as the bicarbonate. 87.5 per cent. of the ammonia may be recovered as the nitrate; alternatively after distillation with lime a product may be obtained having the composition 79.42 per cent. $\text{Ca}(\text{NH}_3)_2$ and 20.58 per cent. NaNH_3 . This substance, of course, should have a high manurial value.

The German Patent, 164,726, directs the electrolysis of the effluent after-mixture with concentrated brine. Owing, however, to the precipitation of lime in the pores of this diaphragm this was not successful.

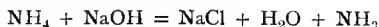
Finlay (English Patent 16,853, 1907, D.R.P. 216,265), in order to recover ammonia and chlorine, submits the ammonium chloride formed in the process to electrolysis, more sodium chloride being added if required. Loss of nitrogen, and in consequence of ammonia, during the operation, however, renders this process impracticable.

Clemm (English Patent 16,470, 1913) treats the ammoniacal mother liquors with an electrolysed solution of brine in order to expel the ammonia. The caustic soda reacts, of course, with the ammonium chloride to regenerate salt. This resulting solution is again electrolysed and used as before. Only a very low concentration of hydroxyl ions is aimed at during electrolysis in order that the current efficiency may be high.

The patentee claims that in this way a perfect process is obtained, and loss of sodium chloride is avoided. It is indeed impossible to conceive how such an extraordinary claim can be justified. It must be at once apparent that the utilisation of sodium chloride in the process is determined entirely by the carbonating operation, and can be in no way dependent on the distillation of the mother liquors. In such a process as that aimed at in this patent, after the distillation of a certain amount of mother liquor, the resulting effluent is again electrolysed, and used for the treatment of a further quantity of the mother liquor, with the result that the amount of liquor in circulation through the ammonia stills will increase indefinitely, and in a plant producing 1,000 tons of soda ash per week the amount of liquor thus circulating at the end of the first week would be in the region of seven million litres. It is, of course, quite impossible to carry out a process of this nature.

It would appear that what is in the mind of the patentee must be in reality the regeneration of the sodium chloride by distillation of the mother liquors with electrolysed brine, and the subsequent treatment of this sodium chloride again in the absorber and carbonating plant (although no indication of such a claim appears in the patent).

It must, however, be remembered that the reaction—



leads to a dilution of the sodium chloride, so that the solution of salt obtained will not be saturated. Further, it would be necessary to produce by electrolysis such a quantity of caustic soda and chlorine as would be equivalent to the whole of the sodium carbonate produced, with the consequence that a much more direct and economical process for the preparation of sodium carbonate would be to carbonate the caustic alkali during electrolysis as in the Hargreaves Bird cell.

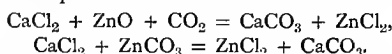
It is unnecessary to point out further defects in such a patent as applied to the ammonia soda industry, although they are many.

By-Products of the Ammonia Soda Process.—Although it has often been pointed out that the longevity of the Leblanc process has been due to the recovery of by-products, and that in this respect it has an advantage over the ammonia soda process, yet in reality this advantage is not very great, for while the Leblanc process can point to bleaching powder, sulphur, and hydrochloric acid, the Solvay process can point to chloride of ammonia, carbonate of ammonia, liquid ammonia, and calcium chloride.

The outstanding defect in the ammonia soda process is the fact that practically the whole of the chlorine originally present in the brine is run to waste as calcium chloride. A small quantity of this material is recovered and used for dust-laying, refrigerating, and other purposes.

By means of this calcium chloride Messrs Brunner, Mond, & Co. prepare metallic zinc.

Calamine suspended in a solution of calcium chloride is treated with a current of carbon dioxide when the following reactions take place :—



The zinc is subsequently recovered from the chloride by electrolysis. Difficulties were at first experienced in obtaining a coherent deposit of zinc, but these have now been overcome.

Numerous attempts have been made in various directions to recover the chlorine present in the calcium chloride as such, but so far no economical method has been found.

Soda Crystals.—A large amount of sodium carbonate finds its way into commerce as the decahydrate ($\text{NaCO}_3 \cdot 10\text{H}_2\text{O}$) and is known as soda crystals or washing soda. It is very largely used where a mild form of alkali is required.

Soda ash, produced by the ammonia soda process, is dissolved with the aid of steam and a mechanical agitator in a mild steel vessel; a small quantity of salt cake is also added to harden the crystals. The solution is made of such a strength that it has a specific gravity of about 1.2–1.3 at 100° C. It is then passed into settling tanks, where the liquor is treated with bleaching powder in order to oxidise any organic matter that may be present and so decolorise the solution. Also in this way any iron present will be converted into the ferric state. Subsequently milk of lime is added, and any iron precipitated. At the same time the calcium carbonate produced, in falling to the bottom of the settling vat, carries with it other suspended matter of lower density. After standing for several hours the clear liquor is syphoned off into large mild steel semicircular crystallising pans, which usually hold from 8–10 tons of soda crystals. Flat bars are placed on the top of the pan and lie in the liquor in order that the crystals forming on the surface of the solution may be supported. The process of crystallisation usually takes about seven days in the winter and ten days in the summer. At the end of this time the mother liquor is allowed to drain away, and the crystals are crushed and subsequently treated in a hydro-extractor. The finest crystals are those formed on the surface of the liquor.

A very large amount of space is required for the production of soda crystals, owing to the length of time which the liquor must remain in the crystallising pans. In consequence a large number of patents have been taken out to expedite the process of cooling by using artificial means. Cf. Mactear (English Patent 10,651, 1884), Dekher (English Patent 24,978, 1898), Kunstner (English Patent 5,808, 1900). In this way, however, only small crystals are obtained, and although in this form the product is equally well, in fact better, suited for the purposes to which soda crystals are put, doubtless owing to prejudice on the part of the consumer, it is not widely used in this country. On the Continent, however, considerable quantities are produced.

Crystal Carbonate.—When a hot solution of sodium carbonate is allowed to evaporate, fine crystals, having the composition $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, are deposited. This monohydrated carbonate of sodium is placed on the market under the name of “**crystal carbonate**.” It contains 81.5 per cent. Na_2CO_3 , 17.73 per cent. H_2O , as compared with the decahydrate, which contains 36.7 per cent. Na_2CO_3 and 62.86 per cent. of H_2O . The dissolution of the monohydrate in water results in the evolution of heat, whilst in the case of the decahydrate the action is endothermic.

At about 300° C. ordinary soda crystals dissolve in their water of crystallisation, whereas the monohydrate does not melt below a red heat, with the consequence that crystal carbonate finds application in tropical countries. Further, for export purposes especially, the lower cost of carriage per unit of alkali is of course an advantage.

Bicarbonate of Soda.—The sodium bicarbonate produced in the ammonia soda process contains a small quantity of ammonia which renders it unfit for many of the purposes to which the pure product is put. In order to produce the refined article the ammonia may be expelled from the crude product by a preliminary roasting operation. A large quantity of carbon dioxide is, however, lost in this way and it will in consequence be necessary to recarbonate the product so obtained after dissolution in water (C. F. Brock and Hawlickek, English Patent 8,314, 1896).

The bicarbonate of soda which separates out is filtered in the usual way and most of the moisture removed in a hydro-extractor; finally in a current of hot air or CO_2 (C. F. Jarmay, English Patent 3,889, 1893). The product is dried, then subsequently ground to an impalpable powder.

The expulsion of the ammonia from the crude bicarbonate of soda may also be effected whilst it is in solution or suspension by means of steam; recarbonation of the resulting liquors will, however, be necessary (C. F. Solvay, English Patent 173, 1888; Jarmay, English Patent 23,890, 1893).

Amongst other methods for the preparation of pure bicarbonate of soda may be mentioned that patented by Mond and Jarmay (English Patent, 2,996, 1884), who direct the dissolution of the crude salt in water at 65°C . After filtration and cooling, pure bicarbonate of soda separates out, leaving all ammonium salts in solution.

Concentrated Crystal Soda, Sodium Sesquicarbonate (Watts and Richards, English Patent 13,001, 1886).—This substance ($\text{Na}_2\text{CO}_3\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is prepared by allowing a solution containing suitable proportions of the normal and acid carbonates of sodium to crystallise above 35° . It finds application in wool washing and possesses the advantages of being neither efflorescent nor deliquescent.

CHAPTER VII

The Stassfurt Industry

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CHAPTER VII

THE STASSFURT INDUSTRY

LITERATURE

- DAMMAR.—“Chemische Technologie.”
 — “Chemische Technologie der Neuzeit.”
 OST.—“Chemische Technologie.”
 THORPE.—“Dictionary of Chemistry.”

The Stassfurt Industry

THE Stassfurt deposits were discovered in the year 1839, and have proved of vast importance technically as the source of a large quantity of the potassium salts of commerce, besides magnesium and sodium salts.

The following minerals are found :—

Mineral.	Formula.
Rock salt	NaCl
Anhydrite -	CaSO_4
Polyhalite -	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Carnallite -	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Boracite (Cryst.)	$2\text{Mg}_3\text{B}_8\text{O}_{15} \cdot \text{MgCl}_2$
Douglasite-	$2\text{KCl} \cdot \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$

These are the originally deposited minerals. By their decomposition the minerals given below are formed and are accordingly found in the deposits.

Mineral.	Formula.
Sylvin	KCl
Kainite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Schönite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
Tachhydrite	$\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$
Bischofite	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
¹ Krugite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Reichardtite (Epsom salts)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
¹ Glauberite	$\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$
Astrakanite	$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$
¹ Pinnoite	$\text{MgB}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$
Hydroboracite	$\text{CaB}_2\text{O}_4 \cdot \text{MgB}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is also found in the upper strata.

From the first discovery of them the nature and composition of the deposits has aroused great interest. Great numbers of experiments have been done with a view to determining the origin of the deposits. The question is a very complicated one, and much valuable work was done on it by van't Hoff. It can only be referred to very briefly here, as the question is one of pure chemistry rather than of great technical importance. It has been found that pressure and temperature have a great influence upon the salts deposited from a mixture.

¹ These minerals are decomposed by water.

For example, from a solution saturated with sodium chloride at 25° C., and also containing magnesium chloride, potassium sulphate, magnesium sulphate, and potassium chloride, the following are obtained :—

Name.	Formula.
Rock salt	NaCl
Sylvin -	KCl
Carnallite -	KCl. MgCl ₂ . 6H ₂ O
Magnesium sulphate	MgSO ₄ . 6H ₂ O
„ „	MgSO ₄ . 7H ₂ O
Magnesium chloride	MgCl ₂ . 6H ₂ O
Schönite	K ₂ SO ₄ . MgSO ₄ . 6H ₂ O
Glaserite -	K ₂ . Na(SO ₄) ₂
Magnesium sulphate	MgSO ₄ . 5H ₂ O
„ „	MgSO ₄ . 4H ₂ O
Sodium sulphate	Na ₂ SO ₄
Astrakanite	Na ₂ SO ₄ . MgSO ₄ . 4H ₂ O

By varying the temperature and pressure can be obtained also—

Kieserite	MgSO ₄ . H ₂ O
Kainite	K ₂ SO ₄ . MgSO ₄ . MgCl ₂ . 6H ₂ O

With this brief general survey of the deposits we can pass to a more detailed account of the various salts.

Carnallite (MgCl₂. KCl. 6H₂O).—Carnallite or potassium magnesium chloride is the mineral from which most of the potassium chloride of commerce is obtained. It is of a red colour, due, according to Ruff, to anhydrous ferric oxide. Sp. gr., 1.6; hardness, 1 (Moh.); greasy, shining lustre; colour, white, pink, or red; gives a conchoidal fracture; intumesces when heated; easily soluble in water.

Carnallite contains a minimum of 9 per cent. potassium chloride, which is obtained from it in the following manner :—

By dissolving the crude salt in the hot mother liquors (*vide infra*) and allowing to crystallise, a product containing 80-85 per cent. potassium chloride is obtained. This method of manufacture is still much used.

Several other methods of treating the carnallite are also in operation (see Potassium Salts).

By the electrolysis of fused carnallite metallic magnesium is obtained.

Kainite (K₂SO₄. MgSO₄. MgCl₂. 6H₂O).—Kainite is sold under a guarantee as containing 12.4 per cent. potassium oxide. Sp. gr., 2.13; hardness, 2 (Moh.); vitreous lustre; colourless, grey, or yellow crystals; soluble in water.

It is used as a source of potassium sulphate, which is prepared from it by the method of Precht, which consists in heating the mineral with a saturated solution of potassium magnesium sulphate and sodium chloride under a pressure of 2-4 atmospheres. The double salt (K₂SO₄. 2MgSO₄. H₂O) separates and is filtered off and washed. By this washing, 1 molecule of magnesium sulphate is removed, and the residue (K₂SO₄. MgSO₄) comes into the market as potassium magnesium sulphate. By treating these with potassium chloride, potassium sulphate can be obtained.

Another method of separating the potassium as potassium sulphate, or as potassium sodium sulphate, consists in the use of ammonia, whereby the magnesium is separated as the double ammonium chloride. Enough ammonia is first led in to combine with half the magnesium, the magnesium hydrates are filtered off and the filtrate saturated with ammonia. The magnesium now remains in the solution as the double salt, and the potassium sulphate separates.

Magnesium chloride is obtained from the mother liquors of the above salts. These contain 28-29 per cent. magnesium chloride with about 0.3 per cent. magnesium bromide. This latter is separated and used for the preparation of bromine.

The liquors are concentrated to a specific gravity of 1.388-1.401, and on cooling this MgCl₂. 6H₂O crystallises out (see Magnesium Salts).

Kieserite (MgSO₄. H₂O).—Sp. gr., 2.5-2.6; hardness, 3; vitreous lustre; white, yellow, or grey crystals; easily fusible; soluble in water. Kieserite is used as

the source of Epsom salts, or magnesium sulphate heptahydrate. This is obtained by long boiling of the kieserite with water.

Glauber Salt.—This salt, well known for its medicinal properties, is obtained at Stassfurt by working up residues from the carnallite (see table).

These have the following composition :—

NaCl	45.55 per cent.
KCl	3.5 "
MgCl ₂	3.4 "
MgSO ₄	25.30 "
CaSO ₄ and insoluble matter	7.9 "
Water	7.10 "

These are allowed to stand some time in the air, and are then dissolved to make

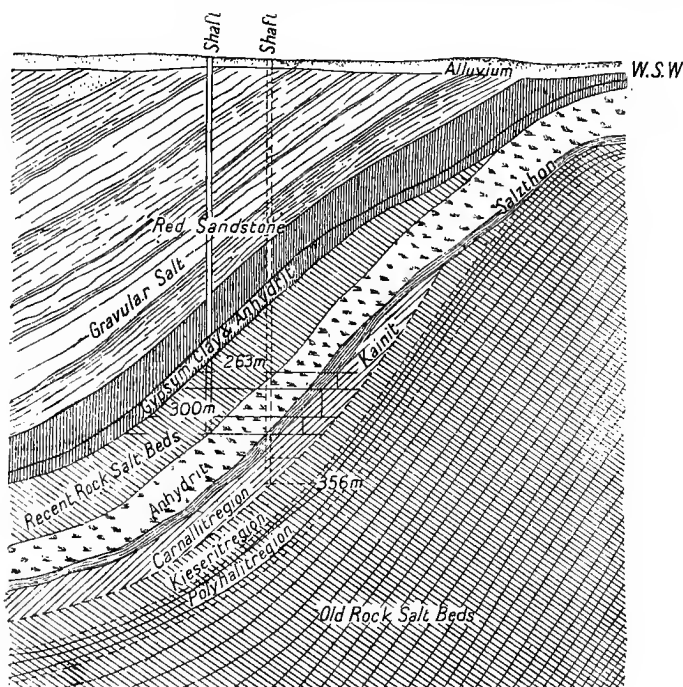
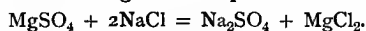


FIG. 36.—Stassfurt Salt Deposits.

a solution of specific gravity 1.268-1.29 at 33° C., which contains about 150 kg. magnesium sulphate per cubic metre. This solution is allowed to spontaneously evaporate in flat crystallising pans.

Glauber salt is formed according to the equation :—



The crude crystals are drained and recrystallised, and dried at 25°-30° C.

Boracite.—The following minerals are classed together under the name of Boracite :—

Boracite	$2\text{Mg}_2\text{B}_3\text{O}_{13} + \text{MgCl}_2$
Hydroboracite	$\text{CaMgB}_4\text{O}_{10} \cdot 6\text{H}_2\text{O}$
Pinnoite	$\text{MgB}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$

These are found in lumps in the deposits of carnallite and kainite. They are

sparingly soluble in water and can be obtained by washing out the more soluble portions of these salts.

The percentage of Boracite is from .0112-.045.

The residue from the working up of carnallite, etc., contains about 15 per cent. boracite.

Boric Acid is obtained from these boron-containing minerals by precipitation with hydrochloric acid. 100 parts boracite require 150 parts hydrochloric acid and 300 parts water. From 100 parts boracite, 82.85 parts crystalline boric acid are obtained.

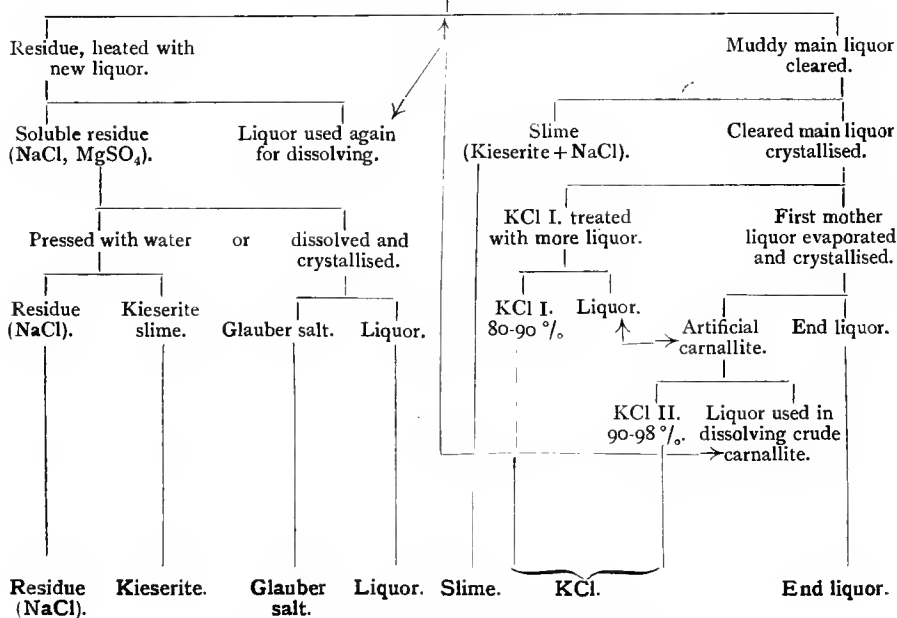
The "end liquor" of the potassium salt manufacture contains much magnesium chloride, for the preparation of which see Magnesium Salts.

A small amount of magnesium bromide is contained in the magnesium chloride.

The end liquor contains from .287-.323 per cent. MgBr_2 . This corresponds to about 3.5 kg. bromide per cubic metre. The bromine is separated by treatment with chlorine as described under **Bromine** in Martin's "Industrial Chemistry," Vol. II.

Treatment of Carnallite

Crude carnallite heated with crude liquors.



STATISTICS OF SALT FROM 1898 TO 1907

Salt.	1898.	1899.	1900.	1901.	1902.
	Tons.	Tons.	Tons.	Tons.	Tons.
Potassium chloride	191,347	207,506	271,512	294,666	267,512
Magnesium chloride	19,819	21,370	19,397	21,018	19,658
Glauber salt	69,111	79,062	90,468	76,066	90,742
Potassium sulphate	18,853	26,103	30,853	37,394	28,278
"Magnesium"	13,982	9,765	15,368	15,612	18,147
Magnesium sulphate	30,295	39,540	48,591	46,714	39,262
...	35,366	37,693	44,372	46,807	47,905
Alum	4,069	3,358	4,355	4,145	4,108
Total	382,842	424,397	524,916	542,422	515,612

Statistics of Salt from 1898 to 1907—continued.

Salt.	1903.	1904.	1905.	1906.	1907.
	Tons.	Tons.	Tons.	Tons.	Tons.
Potassium chloride	280,248	297,238	373,177	403,387	473,138
Magnesium chloride	22,990	25,730	29,017	38,468	32,891
Glauber salt	83,087	76,034	68,455	81,175	80,340
Potassium sulphate	36,674	43,959	47,994	54,490	60,292
"Magnesium"	23,631	29,285	34,222	35,211	33,368
Magnesium sulphate	37,844	39,312	58,568	42,041	41,105
... ..	49,727	55,481	55,806	55,969	59,473
Alum	3,934	3,850	4,270	4,494	4,200
Total	538,135	571,389	671,509	715,235	784,814

CHAPTER VIII



Potassium Salts

CHAPTER VIII

POTASSIUM SALTS

LITERATURE

“The World’s Supply of Potash.” The Imperial Institute, London, 1915.

THE great commercial importance of potassium salts is so self-evident that it needs no comment.

The chief of these salts are:—**The chloride, sulphate, nitrate, carbonate, bicarbonate, hydrate and chromate.**

Potassium salts of various kinds are found in many mineral deposits, the most notable of which are the Stassfurt deposits (*q.v.*), and the various saltpetre beds of the world, chief among which are those of Ceylon.

These mineral sources can be classed together as inorganic sources, but one great branch of the potassium industry consists in the manufacture of potassium carbonate from vegetable or organic sources.

The most important, perhaps, of all the various manufactures is the preparation of **potassium chloride** from the **Stassfurt deposits**.

It is prepared from **carnallite** in the following manner:—

The crude ore, containing usually about 16 per cent. KCl, is first of all dissolved, usually in the “end liquor” (see table, p. 86), which itself contains 10-20 per cent. of magnesium chloride. This liquor is kept at boiling temperature (approximately 115° C.) during the solution. When the maximum amount of ore is dissolved, the hot liquor is run off from the insoluble kieserite and mud into clearing vats and is allowed to stand (still being kept hot) for an hour or two. If necessary the specific gravity of the solution is reduced to 1.28-1.30 before clarifying.

The clarified liquor is then run off into crystallising vats, and allowed to cool fairly slowly. It is allowed to crystallise for two or three days.

Fig. 37 shows the plant used in working up the carnallite for KCl manufacture. The raw carnallite is coarsely ground in the mill *a*, then transferred by the elevator *b* to the dissolving boiler *d*, made of cast iron and fitted with a perforated false bottom, on which the carnallite rests. The capacity of the boiler is usually 12 cub. m. It is fitted with steam-heating coils and a valve for running off the contents, also manholes, etc. The liquor used for lixiviation (usually the “end liquor”) is pumped from *g* (by the pump *h*) into the heating tank *i*, thence it flows into the boiler *d*, where it is heated to about 115° C., the boiling being continued for some time until as much salt is dissolved as possible, the crude carnallite being added gradually to the hot liquor. There remains behind a mud of kieserite, lumps of hard rock salt, etc. The hot solution flows away through the filtering tank *e* (where much of the mud is retained) into the clarifying tank *f*; and, after clarifying, is run hot into iron crystallising tanks, where crystallisation of the KCl I. takes place.

These crystals (potassium chloride I.) contain after drying 80-85 per cent. KCl.

These are washed several times with water or weak liquor, and finally attain a concentration of about 90 per cent. KCl.

The mother liquor from the crystallisation of the KCl yields on further evaporation “artificial carnallite.” This is dissolved in the washing liquors and crystallised. It yields a potassium chloride of 90-98 per cent. purity after washing as before and drying. The final washing liquors serve as a solvent for the crude carnallite.

The composition of the potassium chloride I. is approximately :—

KCl	85	per cent.
NaCl	12	"
MgCl ₂	.05	"
MgSO ₄	.6	"
Water	2.5	"

Potassium chloride is also prepared from sylvine (KCl and NaCl) in the same way as from carnallite, and yields crystals of 92-94 per cent. purity, which after washing and drying are 98 per cent. pure. 100 g. water dissolve 33.4 g. KCl at 15° C., and 56.6 g. at 100° C.

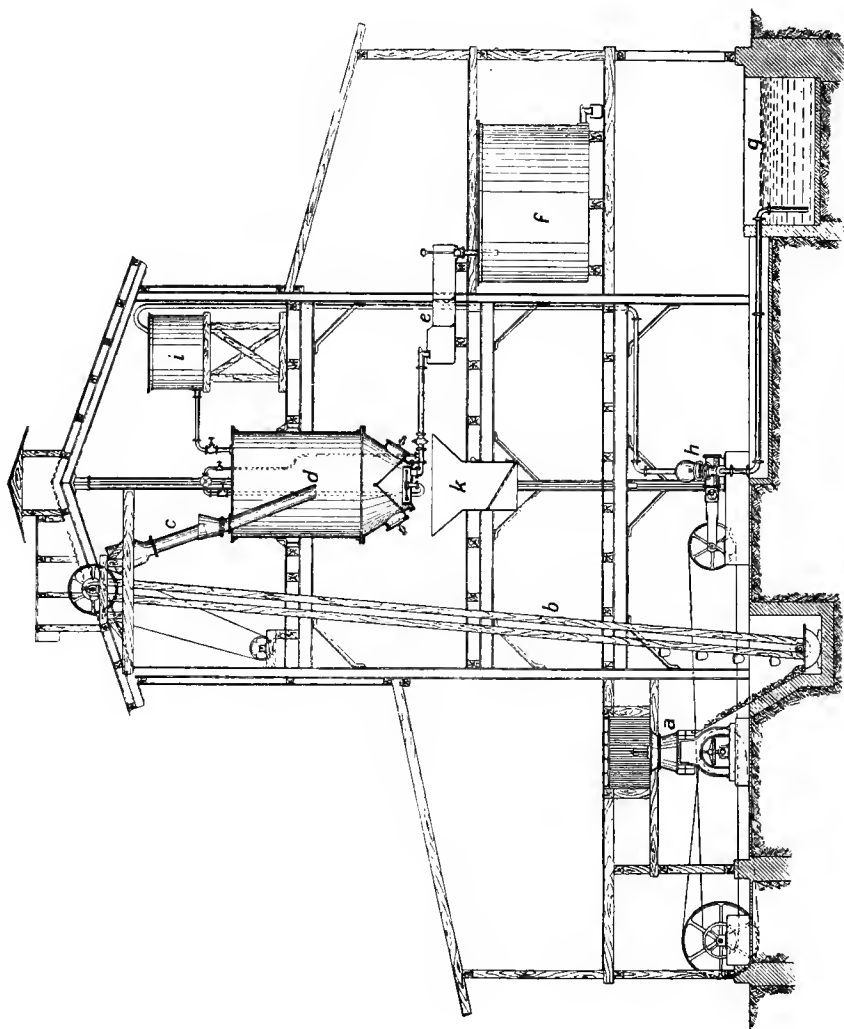


FIG. 37.—Carnallite Plant for KCl Manufacture.

Various patents on these processes are :—

D.R.P. 92,812 of 6th August 1896.
 D.R.P. 98,344 of 13th November 1896.
 D.R.P. 99,957 of 1st December 1896.
 D.R.P. 102,075 of 15th October 1897.
 D.R.P. 129,864 of 16th April 1901.
 D.R.P. 128,999 of 14th March 1901.

D.R.P. 135,722 of 14th November 1899.
 D.R.P. 149,435 of 23rd February 1904.
 D.R.P. 166,558 of 1st June 1904.
 D.R.P. 132,474 of 18th June 1901.
 D.R.P. 206,410 of 2nd October 1907.
 D.R.P. 207,887 of 28th March 1907.

And many others.

Potassium Sulphate (K_2SO_4)

Kainite ($K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$) is chiefly used as the starting point in this manufacture.

It is finely ground and macerated with water, and allowed to stand in the air for some time. It then separates into potassium magnesium sulphate and magnesium chloride liquor.

In modern times, however, Precht's method is followed, viz.:—

The crude kainite is heated with a saturated solution of common salt and potassium magnesium sulphate under a pressure of 2-4 atmospheres.

Precht's double salt ($K_2SO_4 \cdot 2MgSO_4 \cdot H_2O$) is thus formed. It is separated and dried at $100^\circ C.$, and is practically pure, after washing.

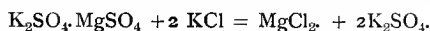
(The mother liquor from this crystallisation contains KCl and $MgCl_2$ and can be used in the working up of carnallite.)

Crude kainite yields 30-40 per cent. of potassium magnesium sulphate.

The washing liquors on evaporation yield **Schoenite**, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$.

Schoenite can also be prepared by the interaction of crude carnallite with kieserite. For this purpose the powdered carnallite is shaken with a hot saturated solution of kieserite.

For the preparation of **potassium sulphate** the potassium magnesium sulphate, prepared in either of the foregoing ways, is macerated with potassium chloride solution of 1.142 sp. gr. ($18^\circ B\acute{e}$.), or else the solution of the double salt is shaken with finely powdered dry potassium chloride—



The crystalline magma of potassium sulphate formed is purified by washing. It is of about 90 per cent. purity before drying and about 96 per cent. after drying. 100 g. water dissolve 10.3 g. K_2SO_4 at $15^\circ C.$, and 26.2 g. at $100^\circ C.$

Potassium Carbonate (K_2CO_3)

Potassium carbonate (K_2CO_3) crystallises anhydrous. 100 g. water dissolve 110 g. K_2CO_3 at $51^\circ C.$ and 156 g. at $100^\circ C.$ It can be manufactured from the following sources:—

1. Mineral—

(a) From potassium chloride and sulphate.

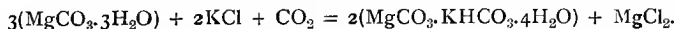
(b) From felspar and other naturally occurring potassium silicates.

(a) (i) For the **Leblanc process** see p. 41.

(ii) The **ammonia process** (p. 51) is not applicable owing to the solubility of potassium bicarbonate.

Ortlieb (D.R.P.'s, 5,706, 9,376, 13,397) used trimethylamine. The great solubility of the hydrochloride of this base admits of the separation of the potassium bicarbonate. This ingenious process was, however, given up after working for a short time.

(iii) **Precht's magnesia process**.—In this process, kiln gases are passed into a paste consisting of a solution saturated at $20^\circ C.$ of potassium chloride mixed with trihydrated magnesium carbonate ($MgCO_3 \cdot H_2O$). The following reaction takes place:—



The double salt formed is washed free from chloride by a solution of magnesium carbonate, and is then heated under pressure at $140^\circ C.$, when it suffers decomposition thus:—



For this process see D.R.P.'s, 55,182, 125,987, 143,594, 155,007, 172,313 and others; also R. Engel, D.R.P. 15,218.

(b) Hart (U.S. Pat. 997,671) extracts the potash from silicious minerals by fusing with barium sulphide, and extracting the potassium salt with acid.

2. Vegetable—

- (a) From wood ashes.
- (β) From beetroot molasses.
- (γ) From kelp.

(a) Potassium being a constituent of the ashes of plants, potassium carbonate has been prepared from this source for a very long time.

The following table gives the percentage of potash and ash in some common woods :—

	Per Cent. Ash.	Per Cent. Potash.
Pine	0.34	0.045
Beech	0.58	0.145
Ash	1.22	0.074
Oak	1.35	0.153
Willow	2.80	0.288
Elm	2.55	0.390
Vines	3.40	0.550
Ferns	3.64	0.626

In Canada most potash is made from elm, birch, larch, and maple.

The wood is buried in pits dug in the earth and sheltered from the wind.

The ash is collected, spread out in thin layers, sprinkled with water, and worked about until evenly damp.

The damp ash is then placed in casks provided with perforated double bottoms, which are covered with straw, and washed with water many times.

The liquor containing from 20-25 per cent. of salts is then evaporated, and the solid burnt white in a furnace to get rid of organic substances. The yield is about 10 per cent. of the original ashes.

This "wood-potash" contains 50-80 per cent. potassium carbonate, 5-20 per cent. potassium sulphate, also sodium carbonate, potassium chloride and other salts.

(β) **From Beet Sugar Molasses.**—The extraction of potassium carbonate from beet molasses is quite an important branch of the potash industry. Germany manufactures about 15,000 tons yearly. This is manufactured from about 300,000 tons of molasses.

In former times the sugar was got rid of by diluting the molasses, fermenting, and distilling of the spirit.

Nowadays, however, the following method is adopted.

The molasses is neutralised with lime, and concentrated. When syrupy, it is placed on the bed of a reverberatory furnace and carbonised. The heat is carefully regulated, so that the mass does not fuse, as this renders the subsequent extraction with water difficult.

The resulting solid is known in Germany as "Schlempekohle" or in France as "vinasse cinder."

The composition¹ of this is as follows :—

K_2CO_3	30-35 per cent.
Na_2CO_3	18-20 "
KCl	18-22 "
K_2SO_4	6-8 "
Insoluble matter	28-15 "

Vincent (*Compt. Rend.*, 84, 214) runs the liquor at a concentration of 40° Bé. into iron retorts, and distils. The distillate consists of trimethylamine, methyl chloride, ammonia, and other substances of lesser importance.

The working up of the "cinder" is proceeded with as follows :—

The cinder is lixiviated, the liquor being run off when it attains a concentration of 23°-32° Tw. This is then evaporated to 74°-82° Tw. The hot liquid is then allowed to settle for two hours,

¹ For further analyses see also Hinz Fischer's "Jahresberichte," 1893, 389.

during which time potassium sulphate separates along with mud, etc. The clear liquor is then drawn off and allowed to cool. Impure potassium chloride then crystallises.

The mother liquor is evaporated to 127° - 142° Tw. and is slightly cooled, when more potassium chloride separates. On drawing off and cooling, a double chloride of potassium and sodium ($K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$) separates.

This is filtered off and dissolved in hot water, the liquor being then concentrated to 117° Tw. Monohydrated sodium carbonate ($Na_2CO_3 \cdot H_2O$) is separated by fishing.

The mother liquor is boiled down with the former mother liquor from the double carbonate, and after settling is calcined.

Its composition is:—

K_2CO_3	80-84	per cent.
Na_2CO_3	8-10	"
KCl	3-4	"
K_2SO_4	3-4	"
K_2SiO_3 , K_2HPO_4 , and } insoluble matter	0.6-2.2	"

Potassium Bicarbonate ($KHCO_3$)

This is prepared by leading carbon dioxide into a saturated solution of potassium carbonate. The bicarbonate, being much less soluble than the carbonate, crystallises out.

On the manufacturing scale, it is prepared by passing CO_2 into a slightly moistened mixture of "potash" and charcoal.

When all the carbonate is apparently changed into bicarbonate, the mixture is lixiviated with water at a temperature of 70° - 80° C.—not higher, as this would decompose the bicarbonate—and the clear filtered liquor is evaporated to crystallisation.

Potassium Chromate (K_2CrO_4)

For the manufacture of this important potassium salt, chrome-iron ore (Cr_2FeO_4) is used as the starting point.

It is mixed with potash and saltpetre and fused. The mixture is powdered, and the potassium chromate extracted with hot water.

Jacquelain (D. 106, 405; 131, 136) strongly heats the chrome-iron ore with chalk, and decomposes the resulting calcium chromate with potassium sulphate.

According to Massignon and Vatel (Bll. 5, 371; D.R.P. Nr. 56,217), the powdered ore is mixed with chalk, the mixture treated with calcium chloride solution to make a stiff paste, formed into blocks, dried and burnt in a furnace to decompose the $CaCO_3$.

The porous mass is allowed to stand in contact with air until oxidation is complete, then lixiviated, and the residual calcium chromate decomposed with potassium sulphate (or sodium sulphate, sodium chromate is to be prepared).

100 g. water dissolve 62.9 g. K_2CrO_4 at 20° C. and 79.1 g. at 100° C.

Potassium Bichromate ($K_2Cr_2O_7$)

Prepared by roasting finely powdered chrome-iron ore with the purest possible lime and potassium carbonate.

The resulting mixture of calcium and potassium chromates is treated systematically with a solution of K_2SO_4 or K_2CO_3 .

The liquor is mixed with sulphuric acid until of strongly acid reaction, and then evaporated, when potassium bichromate crystallises out. 100 g. water dissolve 13.1 g. $K_2Cr_2O_7$ at 20° C. and 102 g. at 100° C.

Potassium Chlorate ($KClO_3$) is prepared as described under the **Chlorine Industry**, Martin's "Industrial Chemistry," Vol. II.

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